UNIVERSITÉ DE SHERBROOKE
Faculté de génie
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OXYDATION TEMPO DES FIBRES LIGNOCELLULOSIQUES:

UNE NOUVELLE APPROCHE POUR LE TRAITEMENT SILANIQUE EFFICACE

Thèse de doctorat

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Résume

Les matériaux biosourcés ont un intérêt en ingénierie parce qu'ils sont biodégradables et dérivés directement de la nature. De plus, les matières biosourcés sont obtenues à partir de ressources renouvelables comme les plantes (c.-à-d. les fibres cellulosiques comme le lin, le chanvre, le jute, etc.). Les fibres lignocellulosiques sont un bon choix pour renforcer les matrices polymères en raison de leur abondance et de leur prix inférieur à celui des fibres synthétiques conventionnelles. Parmi elles, la fibre de lin est considérée comme un renfort vert alternatif dans les composites polymères en raison de ses bonnes propriétés mécaniques telles qu'une résistance spécifique élevée comparable à celle de la fibre de verre. Malgré tous les avantages de la fibre de lin, ses applications sont limitées en raison de sa nature hydrophile causée par la teneur élevée en holocellulose et la présence de groupes hydroxylés. L'hydrophilicité de la fibre de lin cause une absorption d'humidité élevée qui entraîne une faible adhérence interfaciale, une mauvaise dispersion des fibres dans les matrices et, éventuellement, des changements dimensionnels à l'intérieur des composites. Différents traitements (physiques, chimiques et physicochimiques) ont été effectués pour modifier les propriétés de surface des fibres naturelles. Parmi ceux-ci, l'application d'agents de couplage silaniques, principalement développés pour le traitement de surface des fibres de verre, a été envisagée pour les fibres lignocellulosiques, du fait de la présence de groupes fonctionnels hydroxylés à leur surface Cependant, les agents de couplage silaniques doivent subir une pré-hydrolyse au début du traitement de surface des fibres naturelles en raison de la moindre réactivité des groupes hydroxylés de la cellulose. Les fibres naturelles traitées en surface doivent également être traitées thermiquement à la fin du processus de traitement au silane. Pour éviter ces étapes, la fibre de lin devrait être fonctionnalisée par oxydation sélective des groupes hydroxylés de la cellulose avant le traitement au silane. Cette méthode permet de créer des groupes carboxylés sur la surface de la fibre et d'obtenir une plus forte interaction/liaison avec les molécules de silane. L'effet de l'oxydation sélective sur l'efficacité du greffage des molécules de silane sur les fibres et, par la suite, sur les propriétés physiques et mécaniques de la fibre traitée en surface a été caractérisé. Finalement, des fibres traitées au silane avec et sans oxydation (alcaline-silane et silane oxydé) ont été utilisées pour renforcer une résine bioépoxy. Des essais de flexion et de cisaillement ont été effectués

tandis que l'analyse thermogravimétrique (TGA), l'analyse mécanique dynamique (DMA) et l'absorption d'eau ont été utilisées pour examiner les propriétés physiques des composites.

Les résultats ont montré une augmentation significative des propriétés physiques et mécaniques de la fibre de lin lorsque celle-ci étaint oxydée avant le traitement au silane. De plus, une résistance interfaciale plus élevée et une absorption d'eau plus faible ont été obtenues.

Abstract

Bioresources materials have received the attention in many engineering applications because they are biodegradable and derived directly from the nature. In addition, bio resources materials are obtained from renewable resources such as plants (i.e. cellulosic fibers like flax, hemp, jute, and etc). The lignocellulosic fibers are a good candidates for reinforcing bio-based polymer matrices due to their abundancy and lower price compared with conventional synthetic fibers. Among them, Flax fibers have been considered to be employed as the alternative green reinforcements in polymer composites due to their good mechanical properties such as high specific strength that is comparable to glass fibers. However, despite numerous advantages of flax fibers, their applications are limited due to the hydrophilic nature of the fiber that caused by high holocellulose content of flax and the presence of hydroxyl groups in their structure. Hydrophilicity of flax fibers leads to the high moisture absorption that resulted in the weak interfacial adhesion, poor fiber dispersion within the matrices and eventually, dimensional changes of fiber within the composites. Different treatments (physical, chemical, and physico-chemical) have been applied to modify surface properties of natural fibers. Among them, application of silane coupling agents that primarily developed for glass fiber surface treatment, have been considered for lignocellulosic fibers treatment. This was due to the presence hydroxyl functional groups on the surface of both lignocellulosic and glass fibers. However, silane coupling agents must undergo the pre-hydrolysis process at the beginning of natural fiber surface treatment due to lower reactivity of cellulose hydroxyl groups. Also surface treated natural fibers must be heat treated at the end of silane treatment process.

To avoid above steps, the flax fibers should be functionalized by means of selective oxidation of hydroxyl groups on thecellulose structure to pave the way for the subsequent silane treatment. This method is capable of creating carboxyl groups on the flax fiber surface for the stronger interaction/bonding with silane molecules. The effect of selective oxidation on the bonding efficiency of silane coupling agents and subsequently, on the physical and mechanical properties of the surface treated fiber was characterized. Eventually, silane treated fibers with and without oxidation (alkaline-silane and oxidized-silane) were used to reinforce the bio-epoxy resin. Flexural, and short beam shear tests were carried out to study the mechanical properties and Thermogravimetric analysis (TGA), Dynamic mechanical analysis (DMA), and water uptake were used to examine the physical properties of the composites.

Results showed a significant increase in physical and mechanical properties of flax fibers when the fibers were oxidized before the silane treatment. Moreover, higher interfacial strength and lower water absorption were obtained in comparison with the control ones.

Dedication

To my beloved wife, Sepideh, who always be supportive and gave me the motivation to finish this project and,

To my parents who always encourage me to continue my academic endeavor.

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1. Introduction

1.1. Problematic and Project Definition

Bio-composites are defined as hybrid materials that are reinforced with natural fibers/fillers [1]. The global natural fiber (wood, flax, hemp, cotton, etc.…) reinforced composites' (NFRC) market value is estimated about 4.5 billion USD in 2016. Wood fibers have dominated the major part of the market (around 60% of the whole market) while flax fibers have had a market share of 13% (Figure 1.1)[2].

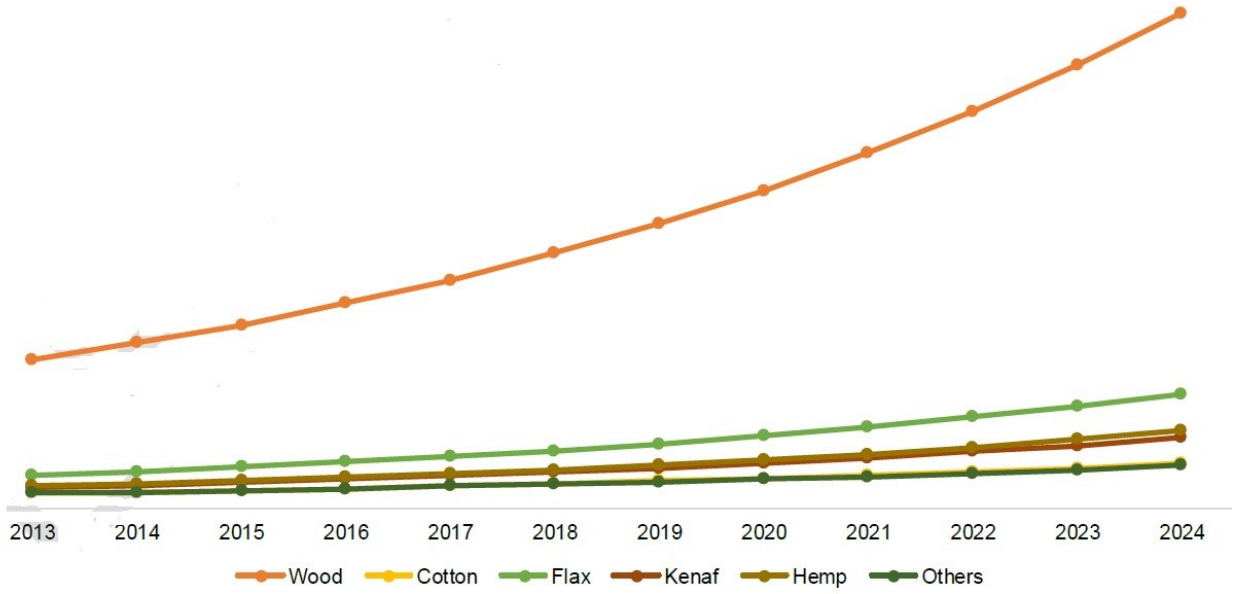

Figure 1.1 Global natural fiber composites market share [2]

Flax fiber is an abundant, bio degradable and renewable material with zero CO_2 footprint compared with synthetic fibers (e.g. carbon and glass). Flax fiber is one of the most used natural fibers in industry because of its specific properties including high specific tensile strength, ultraviolet (UV) blocking and vibration absorbance [2]. Compared with glass fibers, flax fibers demonstrated similar specific properties at a lower price [3]. Flax fiber composites, unlike glass fiber composites, can be combusted for energy recovery without leaving considerable residues [4]. In addition, flax fibers demonstrated low abrasion on tools that is crucial in polymer processes like extrusion and injection moulding [5]. However, natural fibers have some disadvantages that should be handled before using as reinforcements for polymer resins:

1. The properties of natural fibers depend on the condition of cultivation

2. Natural fibers have low thermal resistance and start to degrade at temperatures around 200°C which most of the general purpose plastics are processed;

3. Natural fibers are hydrophilic at high level which results in both, high water absorption and low compatibility with hydrophobic polymeric matrices.

The mechanical properties of natural fibers composites are adversely affected by moisture absorption [6-12]. It is concluded that strong adhesion at composite interface enhances the mechanical performance of the composite and prevents water absorption [10, 13]. Flax fibers' structure consists of cellulose micro fibrils held together by hemicellulose, pectin and lignin [14]. Both cellulose and hemicellulose have hydroxyl groups in their structure that cause high polarity and, subsequently, high tendency to water molecules. Therefore, incorporation of hydrophilic natural fibers into the hydrophobic polymeric matrix leads to poor adhesion between them. Converting hydroxyl groups of the flax fiber into the hydrophobic functionalities would be useful to compatibilize the flax fiber with polymer matrices. Many attempts including chemical and physicochemical treatments have been made for surface modification of natural fibers. The chemical treatments, especially application of coupling agents such as silane treatment, have shown significant improvement in interfacial adhesion between natural fiber and polymer resins [15]. Silane coupling agents, initially developed for functionalization of glass fibers [16], are widely used for the surface modification of natural fibers. Silane coupling agents can react with hydroxyl groups on the fiber surface and alter the surface chemistry. However, because of the lower activity of hydroxyl groups of natural fibers in comparison to glass fibers, they cannot directly react with alkoxysilanes [17]. They should be pre-hydrolyzed in specific pH to form more active silanol groups; then, interact with hydroxyl groups on the fibers` surface via hydrogen bonding. Finally, heat treatment at elevated temperature (≈120 °C) is required to transform the hydrogen bonding between silane molecules and hydroxyl groups into the covalent bonding [15]. The procedure for conventional silane treatment of natural fibers is shown in Figure 1.2.

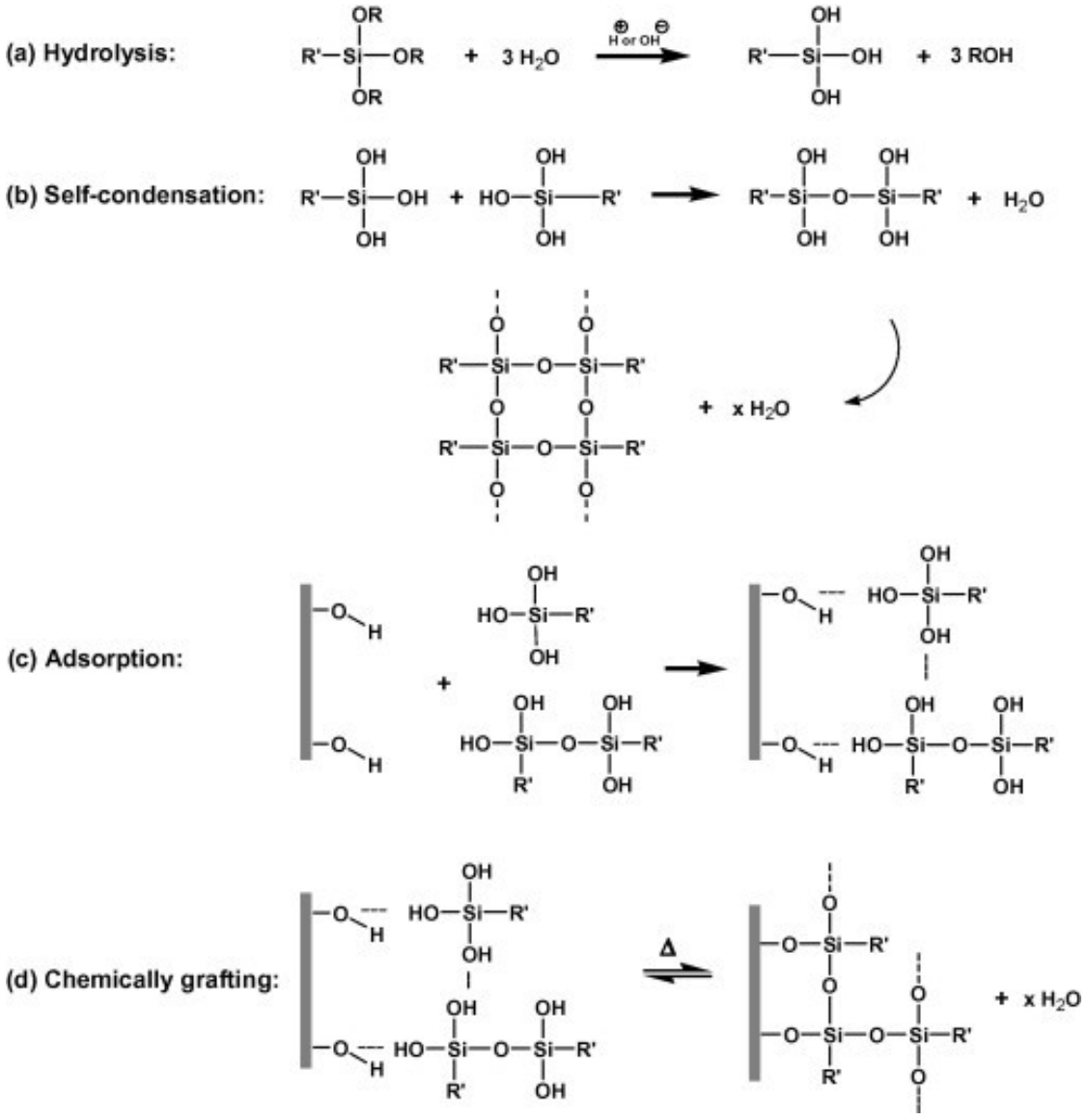

Figure 1.2 Schematic of conventional silane treatment

To avoid those additional steps (pre-hydrolysis and heat treatment), the reactivity of hydroxyl groups on the fiber's surface must be increased. Oxidation of alcoholic OH groups of flax fibers to the more reactive carboxylic acid OH groups, due to the presence of an adjacent carbonyl group , could be an option for this target [18]. An interesting oxidation method for cellulosic fibers is 2,2,6,6-tetramethylpyperidine-1-oxy radical (TEMPO) mediated oxidation. TEMPO mediated oxidation selectively oxidizes primary alcoholic OH groups and produces carboxyl functional groups along with small amount of aldehydes onto the cellulosic fibers (Figure 1.3)[19].

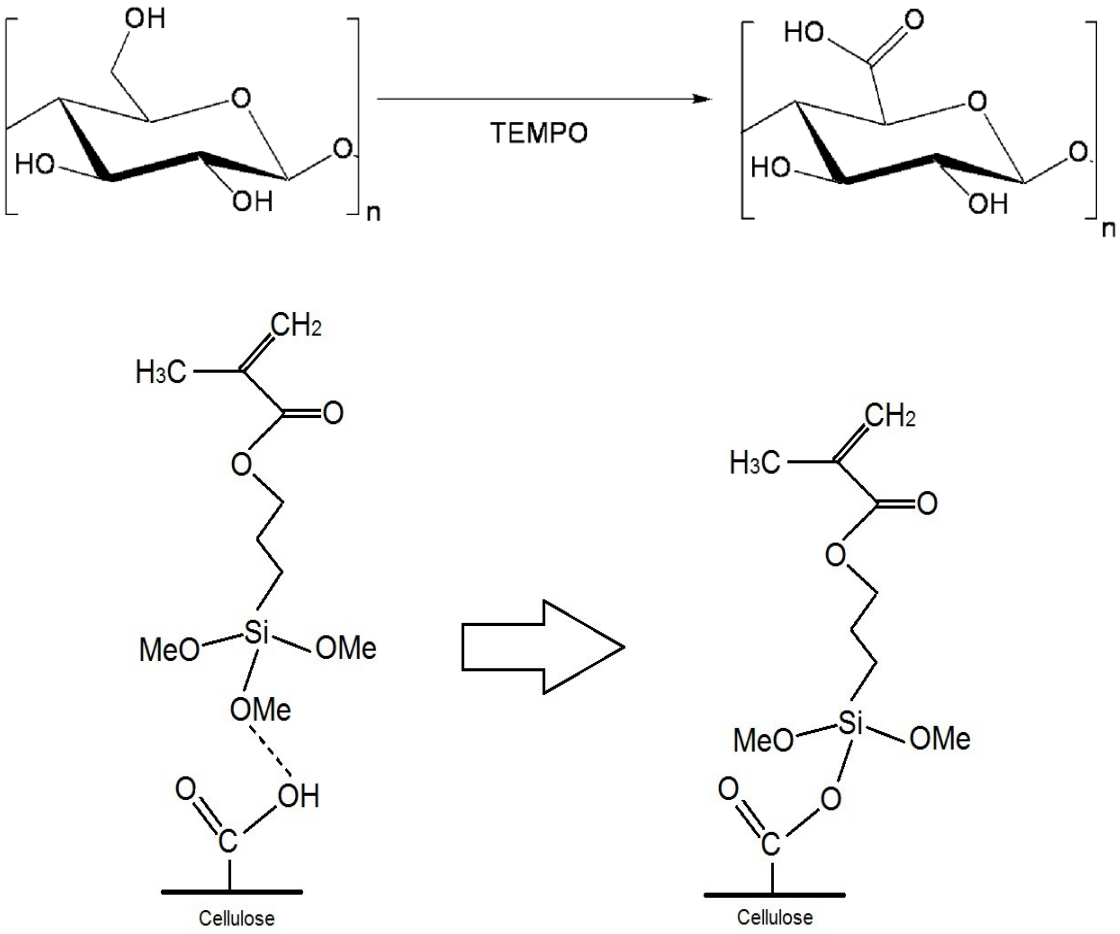

Figure 1.3 Conversion of primary alcohol to COO- (up), mechanism of silane and oxidized cellulose reaction (down)

1.2. Project Definition

The utilization of natural plants fibers as reinforcement in composite materials is an opportunity to promote environmental sustainability through the valorization of agicultural residues like flax straws. Indeed, Canada produces about 1,200,000 tons of flax straw annually of which more than 75 % of them are usually disposed [30]. As stated above, the transformation of primary hydroxyl groups of flax fibers into the carboxylic groups can facilitate the boding of silane molecules without need of pre-hydrolysis and heat treatment. This method decreases the water absorption of the fibers, especially compared to alkali treated fibers, and moreover, increases the compatibility of the fiber with the polymer matrix.

Therefore, the main objective of this project was to introduce carboxylic OH groups on the flax fibers to enhance surface reactivity of the fiber toward the silane coupling agent in order

to modify the interfacial adhesion and hygroscopic properties of the composite. To reach the above objective, two specific objectives were defined in this study.

1. To evaluate the bonding efficiency of silane molecules to the flax fiber through TEMPO oxidation of the fiber

One of the disadvanateges of natural fibers for silane treatment is the low reactivity of hydroxyl groups on the fiber surface (compared to the glass fiber hydroxyl groups). Therefore, a pre-hydrolysis is suggested to transform silane molecules into the more reactive silanol groups followed by a heat treatment to form covalent bonding. However, we can enhance the reactivity of hydroxyl groups on the fiber instead of silane molecules. Hydroxyl groups can be transformed into more active carboxylic groups by means of the oxidation. Unfortunately, most of the conventional oxidation methods, especially using strong acids, significantly deteriorate mechanical properties of lignocellulosic fibers. A successful method for oxidation of flax fibers by means of TEMPO-mediated oxidation of cellulose was optimized for this study [19]. Then, silane coupling agent was directly applied on the oxidized fiber surface. To examine the bonding efficiency of silane molecules on the oxidized fiber, the oxi-silane and alkali-silane treated fibers were washed overnight by a Soxhlet extractor and examined by EDS analysis, FTIR and XPS. Finally, the effect of surface treatments on the mechanical and hygroscopic properties of fibers was investigated.

2. To assess the effect of oxi-silane treatment on mechanical and hygroscopic properties of flax fiber reinforced bio-epoxy resin

The efficiency of direct silane application on the TEMPO oxidized flax fibers was already confirmed. In order to assess the performance of oxi-silane treated fibers in the biocomposite, unidirectional flax fabrics were treated with the same method and the flax/bio-epoxy composite was fabricated by compression molding. It was expected that flax fiber surface modification promoted the interfacial adhesion between the flax fiber and polymer matrix that, subsequently, resulted in an improvement in physical and mechanical properties of the bio-composite such as Inter-Laminar Shear Strength (ILSS) and flexural properties. The composite specimens were made with as received, alkali-silane and oxi-silane treated flax fabric and their mechanical characteristics were analyzed according to the ASTM standards. Also, physical properties such as thermal resistance and water absorption were evaluated.

1.3. Project Outline

This thesis have written based on research papers and includes five main chapters. Chapter 1 briefly presents an introduction about the project and describes the motives and objectives of the work.

Chapter 2 has reviewed the advantages and drawbacks of natural fibers' utilization in biocomposites, methods for modification of natural fibers' properties, and introduces TEMPO mediated oxidation as a method for cellulose modification.

Chapter 3 presents the methodology for chemical modification of fax fibers surface by TEMPO oxidation and the effect of this modification on the bonding efficiency of silane is studied. In addition, physical and mechanical properties of flax fiber are evaluated and compared with the control.

Chapter 4 presents the effect of oxi-silane treated fibers on the physical and mechanical properties of flax/bio epoxy composite. It explains the role of modified fiber/matrix interface on the mechanical and hygroscopic properties of the biocomposite.

Chapter 5 presents a summary of the main results and suggested possible future works.

2. Literature Review

Natural fibers are extracted from different sections of lignocellulosic biomass such as stem, leaf, fruit, and seed. The chemical composition of natural lignocellulosic fibers differs within the various layers of the plant structure and depends on the growing conditions such as acidity of soil, humidity and temperature of the region, extraction methodology, and maturity of plants. The major chemical ingredients of lignocellulosic materials are carbohydrates or poly saccharides including cellulose, hemicelluloses and pectin. These polysaccharides are accompanied by the lignin (a mixture of aromatics) and small amounts of proteins, extractives (e.g. waxes), and inorganic elements that can be found in the ash [20-23].

2.1. Natural Fiber Components

Cellulose is the dominant biopolymer in the world. It is estimated that about 10^{10} to 10^{11} tons of cellulose is annually produced (approximately 50% of the total plant biomass [24]. The chemical formula of the linear structure of the cellulose is $C_6H_{10}O_5$ (Figure 2.1). Anhydro-glucose units form the cellulose that contains the three hydroxyl groups at C-2, C-3 and C-6 positions. The cellulose chains are linked together by b-(1,4)-glycosidic bonds. [25].

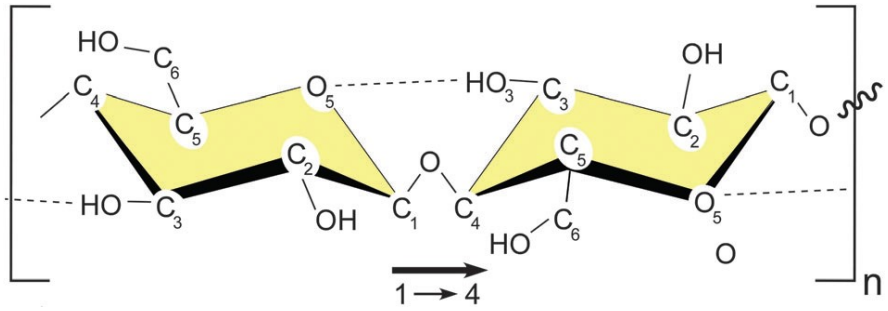

Figure 2.1 Schematic of a cellulose chain repeat unit [25]

2.1.1. Cellulose

Cellulose molecular chains have tended to align through hydrogen bonds between their hydroxyl groups. This chain alignment gives a crystalline structure to the cellulose microfibril. Therefore, natural fibers' stiffness and strength originates from cellulose crystalline structure.

2.1.2. Hemicelluloses

Hemicelluloses are low molecular weight branched hetero-polysaccharides with an amorphous structure that exist in the internal surface of cell walls. Compared to cellulose that contains only D-anhydroglucose, hemicellulose molecular chains are formed by variety of saccharides with lower molecular weight. They act as a matrix component in the natural fibers' structure that cover the cellulose microfibrils [25].

2.1.3. Pectin

Pectin is a high molecular weight polysaccharides with a complex chemical structure that mainly exist in non-wood fibers (e.g. bast fibers). They act as a matrix, like hemicellulose, in the natural fiber cell walls and provide flexibility to natural fibers [26].

2.1.4. Lignin

Lignin is an amorphous and crosslinked biopolymer that consists of aliphatic and aromatic compounds. Lignin gives rigidity and hydrophobic behaviour to the plant fibers. Lignin is produced as a coating around the cellulose microfibrils and hemicellulose/pectin matrix [20, 26].

2.2. Natural Fiber Structure

Cellulose microfibrils are the main structural units in the plant. The fibrils have a layered structure consisting of a thin primary cell wall and a thicker secondary wall (Figure 2.2). The secondary cell wall contains three distinct layers (S1, S2 and S3), which the S1 determines the mechanical properties of the natural fiber. It consists of cellular micro-fibrils that are helically wounded [25]. The mechanical properties of natural fiber depend on several parameters such as the angle between the fiber axis and the microfibrils, the cellulose content of the fibers, and the molecular weight of the cellulose [27].

Morvan et al. [26] studied on the cellulosic and non-cellulosic ingredients across the flax fiber stem. They found that the stem surface mainly composed of pectin and waxes while cellulose has the majority underneath the surface. The cellulose microfibrills are accompanied by pectin and non-cellulosic polysaccharides that act as cement in the flax fiber. Also, lignin is more present in the core tissues of flax stems.

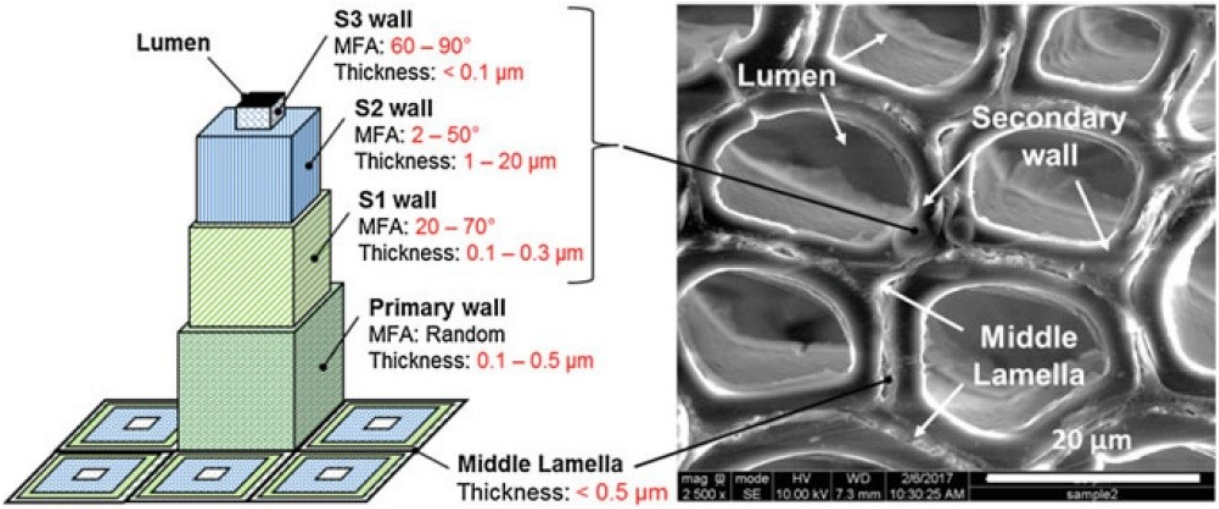

Figure 2.2 Schematic cell wall structure of natural fibers (left) SEM image of wood fiber cells (right) [28]

2.3. Surface Chemistry of Natural Fibers

Natural fibers can be assumed as a bio composite consisting of different ingredients as the matrix that is reinforced by cellulose microfibrills. Each of the bio-composite's components has their own physico-chemical properties which play an important role in the fiber/matrix adhesion during composites manufacturing. Functional groups on the natural fibers surface may be able to interact with the polymeric matrix. These interactions through either hydrogen bonding or covalent bonds could significantly improve the fiber/matrix adhesion. In addition, mechanical interlocking, trans-crystallization of thermoplastics, and cross-linking density of thermoset resins can be modified by the surface characteristics of natural fibers. Thus, in-depth knowledge about the surface chemistry of natural fibers is necessary for better understanding interfacial properties in natural fiber reinforced composites. Schematic of functional groups on the flax fiber surface is depicted in Figure 2.3.

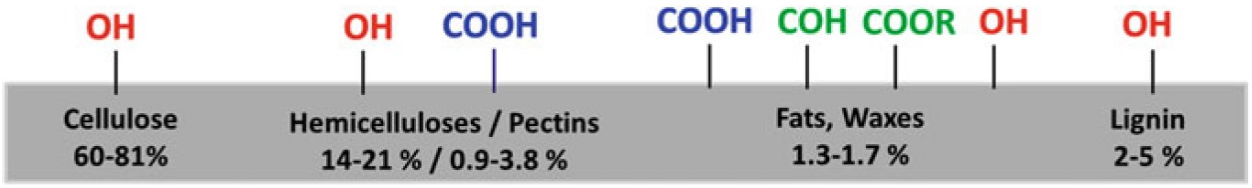

Figure 2.3 Possible reactive functional groups on the flax fiber surface [28]

As shown above, hydroxyl groups show different reactivity, depending on the type of carbon atoms that they bonded (For example, primary and secondary alcohols of cellulose for saturated carbon and phenols of lignin for unsaturated carbons. Carboxyl groups primarily originated from pectin, hemicelluloses, fatty acids at the surface of natural fibers [26, 28]. Natural fibers' surface can also have aldehydes and esters functional groups that originated from their lipophilic components like waxes [28]. In addition, there are some non-cellulosic components on the fiber surface that can be removed during preparation of natural fiber bundles in processes like extraction, separation and conditioning. It is concluded that the surface chemistry of natural fibers has an important role on the reactions occurring on their surface. Also, besides the hydroxyl groups reactions that mainly reported in literature, several side reactions may occur with other functional groups of non-cellulosic components such carboxylic acid, aldehydes and esters [29].

2.4. Role of Fiber/Matrix Adhesion

Natural fibers have been considered as alternatives for synthetic fibers in polymer composites because of their advantages in comparison to synthetic fibers (lower density, zero carbon footprint, lower price, etc.…). However, utilization of natural fibers have been restricted due to their high moisture absorption, poor adhesion with polymer resins, and low thermal resistance. These disadvantages make their surface modification necessary. Indeed, during incorporation of natural fibers into polymer matrices, formation of multiple interfaces should be considered. These interfaces exist within the fiber cell wall layers, within the elementary fibers of the fiber bundles and between the polymer matrix and the elementary fibers or the fibers bundles [30].

Each of these interfacial regions has specific physico-chemical characteristics. Besides, it is well known that interfacial region is a three-dimensional zone (interphase) which develops between bulk matrix and bulk fiber. The interphase includes the contact surface between the fiber and the matrix (interface) and the region that extends from the interface into the fiber and the matrix [31].

Based on above facts, several methods can be used to modify interfacial adhesion in composite materials. Surface free energy of the fibers (polar and dispersive components) can be modified in order to improve the adhesion with the polymer matrix which increases the

fiber wetting during impregnation process. Functionalization of natural fibers enhances their reactivity towards the polymer to form stronger chemical or physico-chemical bonding. The mechanical interlocking phenomena could be enhanced by optimizing the surface roughness/porosity of the fibers.

2.5. Surface Treatment of Natural Fibers

Natural fiber treatments can be categorized into two distinct parts:

1. Pre-treatment that is described as physical or physico-chemical techniques for improving the physical adhesion (mechanical interlocking) between the fibers and the polymer matrix. They disrupt the inter-cellular cohesion within the fiber bundles by the extraction of some non-cellulosic compounds and enhance the fiber dispersion in the polymer matrix. They may also modify the surface roughness or porosity of fibers that leads to higher specific area. Thus, pre-treatments prepare natural fibers for the subsequent chemical or physico-chemical treatments to improve the compatibility with the polymer matrix.
2. Surface modification of natural fibers through the grafting of reactive molecules/polymers by chemical or physical treatments. The grafting/coupling reactions can be directly performed on the as received fibers or pre-treated fibers.

2.6. Pre-treatments of Natural Fibers

The pre-treatments are carried out to make natural fibers ready for utilization in composite materials or for subsequent treatments. Most of pre-treatment methods come from the textile and wood industries that were adapted to modify the quality of lignocellulosic fibers.

2.6.1. Retting Treatments

The retting processes are usually the first step of pre-treatment and performed to facilitate the extraction of fibers from the natural plant fibers stems [32]. Retting treatments degrade the non-cellulosic components that form the cell walls and the middle lamella which stick adjacent plant cells together. Thus, by elimination of these cementing components, fiber bundles cleaves from the surrounding shell [33]. The surface chemistry, fineness and mechanical strength of extracted fibers are greatly depended on conditions of retting processes that comprehensively reviewed by Paridah et al. [34].

2.6.2. Alkaline Treatment

The alkaline treatment (mercerization) is firstly used in the textile industry and defined as a treatment of natural fibers with basic (mostly NaOH) aqueous solutions. Alkali pre-treatments modify the natural fibers by the extraction of the non-cellulosic components (lignin, hemicellulose, and pectin) within the fibers. These components act as a matrix (cement) for the elementary fibers; thus, their extraction can lead to the defibrillation of fiber into elementary fibers or cellulose microfibrils. The alkaline treatment can also modify the crystalline structure in natural cellulosic fibers (usually at concentrations ≥ 15% wt. of aqueous NaOH). In addition, alkaline pre-treatments can increase the hydrophilic nature of the fibers because of the elimination of hydrophobic components from the surface. The removal of hydrophobic (waxes) and non-cellulosic components can enhance the accessibility hydroxyl groups that is beneficial for the possible subsequent chemical treatment. For this reason, alkaline treatments have been considered as pre-treatments for the surface functionalization of natural fibers and their further use in composite materials [29, 35].

2.7. Chemical treatment

Chemical treatment of the natural fibers can modify the fiber' surfaces by reducing the hydrophilicity or the bulk of the fibers by changing the crystalline structure. These modifications can be achieved by several methods such as silane treatment, and acetylation treatment, and polymer/monomer grafting.

2.7.1. Silane treatment

Silane coupling agents are multifunctional molecules that are used to modify the fiber's surface in composite materials. The silane molecules are usually composed of several functional groups that are linked to a silicon atom. There are different types of silane coupling agents; among them, alkxoy silanes are widely used to improve fiber/matrix interaction in polymer composites including natural fiber reinforced polymer composites. To do so, alkoxy silanes usually hydrolyzed to silanols in the presence of moisture. Then, one end of silanol reacts with the cellulose hydroxyl group while the other end reacts with the matrix functional groups. In addition, silane molecules can penetrate into the porous structure

of natural fibers and form an interlocked coating on the fiber surface that leads to better tensile strength properties compared to the alkali treated fiber composites [36].

2.7.2. Acetylation

Acetylation treatment is an esterification method that was originally developed to improve the moisture resistance, dimensional stability, and environmental degradation of wood. However, it seems that neither acetic acid nor acetic anhydride can react sufficiently with the lignocellulosic fibers. To do so, fibers should be impregnated by acetic acid and then treated with acetic anhydride at a higher temperature. During the treatment, the acetyl group (CH_3CO) reacts with the hydrophilic hydroxyl group (OH) of the fiber to alter the hydrophilic nature of the fiber and improve its dimensional stability [37]. Furthermore, it was found that the acetylation decreased the void contents on the fiber`s surface which resulted in higher mechanical interlocking with the matrix [38]. Acetylation reaction with and without acid catalyst on fibers is demonstrated below[39].

$$\text{Fiber-OH} + (CH_3CO)_2O \rightarrow \text{Fiber-O-CO-CH}_3 + CH_3COOH$$

$$\text{Fiber-OH} + CH_3COOH \xrightarrow{(CH_3CO)_2O} \text{Fiber-O-CO-CH}_3 + H_2O$$

2.7.3. Benzoylation Treatment

Benzoyl chloride is the most often used compound that is used for the benzoylation treatment of lignocellulosic fibers. The benzoyl functional group (C6H5C=O) reacts with the hydroxyl groups on the fiber`s surface, decreases its tendency for moisture absorption and improves the fiber/matrix interaction [40]. Benzoylation especially works for the polymeric matrices that bear aromatic functional groups (e.g. Polystyrene). Therefore, benzoylation increases the strength of the composite, decreases its water absorption, and improves its thermal stability.

2.8. Oxidation treatment of cellulosic fibers

As mentioned above, there are various methods for the functionalization of the cellulose in order to increase the compatibility of the lignocellulosic fibers with polymeric matrices. Among them, the surface treatments with the minimum adverse effects on the mechanical properties of the fiber are the most interesting.

Lignocellulosic fibers can be functionalized by oxidizing the hydroxyl groups of the cellulose into the much more reactive carboxyl groups. There are two types of hydroxyl (OH) groups in the cellulose structure, secondary alcoholic OH groups on the C2 and C3 carbon atoms and primary alcoholic OH groups on the C6 atom (**Error! Reference source not found.**2.1). In general, primary alcohols are more reactive than secondary alcohols and can be oxidised into carboxylic acids (or into aldehydes if the oxidation process isn't completed) while secondary alcohols tend to be oxidized into ketones (**Error! Reference source not found.**2.4) [41].

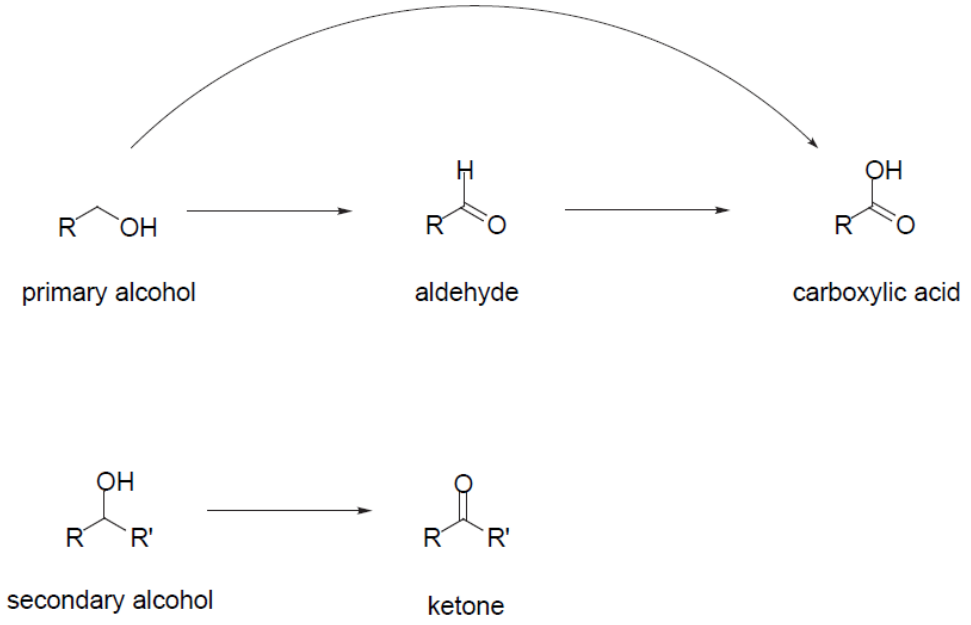

Figure 2.4 Schematic mechanism of oxidation of primary and secondary alcohols [39]

There are two main categories of reactions for the oxidation of hydroxyl groups of the cellulose: selective and non-selective oxidation. Non-selective oxidation usually generates more carboxyl groups compared to selective oxidation. However, due to the nature of this oxidation, the oxidation products are unpredictable. Also, it drastically reduces mechanical properties of fibers because of bearing strong oxidative agents.

In contrast, by means of selective oxidation, we can selectively oxidize the primary or secondary alcoholic hydroxyl groups of the cellulose through two different methods:

In the protection-oxidation method, the alcohol groups that shouldn't be oxidized are covered by protective groups and then oxidizing agents react with desired alcohol groups. The isolated groups become accessible at the end of the oxidation reaction [42].

A second procedure, chemo-selective agents that have higher activity than both primary and secondary alcohols are employed for the oxidation of a targeted hydroxyl group [43].
Despite several methods that have been suggested for selective oxidation of secondary alcohols, in the presence of primary alcohols, there are few efficient methods for selective oxidation of primary alcoholic hydroxyls in the present of secondary hydroxyls [43, 44].

Among them, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) mediated oxidation has been widely employed for the selective oxidation of primary hydroxyl groups. It is because of the efficient conversion of high molecular weight polysaccharides compared to the enzymatic or metal catalyzed oxidation [45].

2.8.1. Mechanism of TEMPO selective oxidation

The mechanism is based on the oxidation of a TEMPO molecule by sodium hypochlorite to form nitrosonium cation which acts as the primary oxidant. The nitrosonium cations reduce to hydroxyl amines after the oxidation of alcoholic hydroxyls into aldehydes and subsequently carboxyl groups. Then, reduced cations oxidize back to nitrosonium ions by means of sodium hypochlorite as the oxidant and sodium bromide as the co-catalyst to complete the reaction cycle [43, 46]. **Error! Reference source not found.**Figure 2.5 shows a schematic of TEMPO mediated primary alcohol oxidation.

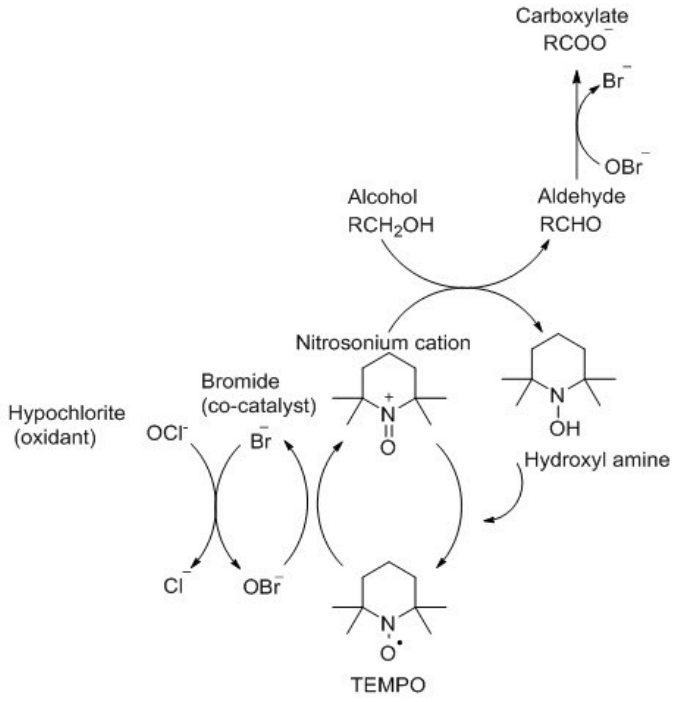

Figure 2.5 TEMPO- mediated selective oxidation of primary hydroxyl groups [46]

2.9. Choice of the matrix for composite manufacturing

As it was already stated, composites have two major components: matrix, and reinforcing elements. Fibers have used in composites in order to increase their strength and stiffness while the matrix component stick the fibers together in order to uniformly transfer the external loads to the fibers [67]. Polymeric matrices may consist of thermosets, or thermoplastic polymers. However, thermoplastic polymers must have two specific requirements to be used as a matrix in natural fiber reinforced composite. The melting point of these polymer should be lower than degradation temperature of the natural fibers and their wettability to the fibers must be sufficient.

Despite thermoplastics, theromoset resins like epoxy are usually liquid at room temperature and their curing temperature can be controlled to prevent exceeding from degradation temperature of natural fibers. Epoxies usually provide excellent chemical, heat resistance along with good electric insulating properties, as well as their mechanical strength. To fabricate a fully biodegradable, eco-friendly composite, in addition to the implementation of natural fibers, bio-based resins should be considered as an alternative for petroleum-based resins. Haq et al. partially replaced unsaturated polyester with epoxidized soybean oil in

manufacturing hemp fiber composites [47]. They found that mechanical properties of the composite decreased but the toughness properties improved. O'Donnell et al. reported similar results when reinforced an acrylated epoxidized soybean oil with the flax and hemp fiber [48]. Partially bio epoxy resins, which a portion of their petroleum-based content replaced by bio based materials, have also demonstrated promising properties in bio-composites applications. In this study, we have used a commercially bio-based epoxies (Super Sap resin by Entropy Resins) with up to 31 % bio-based content (according to USDA certifications) [49].

3. Effect of TEMPO Oxidation of Flax Fibers on the Grafting Efficiency of Silane Coupling Agents

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3.1. Résumé

Les principaux inconvénients de la fibre de lin sont attribués à sa mauvaise compatibilité avec les matrices polymères ainsi qu'à une absorption d'eau relativement élevée, principalement dues à la présence de groupes hydroxylés hydrophiles. Cette étude vise à convertir es groupes alcooliques primaires (OH) à la surface de la fibre en groupes carboxylés par oxydation TEMPO afin d'améliorer l'interaction avec les agents de couplage de silane. La surface des fibres reçues et traitées a été caractérisée par infrarouge à

transformée de Fourier (FTIR) et spectroscopie photoélectronique par rayons X (XPS). Un tensiomètre à angle de contact dynamique (DCA) a été utilisé pour comparer la mouillabilité des fibres oxydées et non oxydées après le traitement au silane. L'interaction entre la fibre de lin et le polymère a été caractérisée par microscopie électronique à balayage (MEB). Les résultats ont indiqué que l'oxydation TEMPO a amélioré de manière considérable la capacité d'adhérence des agents de couplage au silane sur la surface de la fibre. Ainsi, la compatibilité entre la fibre de lin et la résine époxy a été améliorée. De plus, le caractère hydrophile et l'absorption d'eau des fibres modifiées a été remarquablement réduite.

Mots-clés : Fibre naturelle ; oxydation TEMPO ; absorption d'eau ; adhésion interfaciale.

3.2. Abstract

The main drawbacks of flax fibers have been attributed to poor compatibility with polymer matrices as well as relatively high water absorption. The aforementioned properties are mainly due to the presence of hydrophilic hydroxyl functional groups on the backbone of the flax fibers. This study aims to convert primary alcoholic (OH) groups on the surface of flax fiber to carboxyl groups by using TEMPO oxidation in order to facilitate the silane treatment process. Subsequently, carboxyl groups can more easily interact with silane coupling agents. The surface functionality of as received and treated fibers was characterized using Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). Dynamic contact angle tensiometer (DCA) was used to compare wettability of the oxidized and non-oxidized fibers after the silane treatment. The interaction between flax fiber and polymer was characterized using scanning electron microscopy (SEM). The results indicated that the TEMPO oxidation significantly improved the bonding efficiency of the silane coupling agents on the fiber surface. Thus, the compatibility between the flax fibers and the epoxy resin was improved. In addition, the water absorption of the modified fibers was remarkably reduced while the contact angle of the flax fibers was increased.

Keywords: Natural fiber; TEMPO oxidation; Water absorption; Interfacial adhesion.

3.3. Introduction

Renewable materials derived from nature are very attractive for different applications, such as automotive industries and infrastructures, due to their special characteristics namely environmental friendliness, vast availability, cost-effectiveness, and biodegradability (end of life) [50]. Among renewable materials, cellulosic natural fibers (NF) are one of the most promising resources mainly because of their good mechanical properties like their high specific strength [51, 52]. Various types of NF including cotton, jute, hemp, and flax have been used in the production of yarns. Among these fibers, flax fiber is the one in which the mechanical properties (e.g. specific tensile strength) are comparable to glass fibers [53]. It makes flax fiber a perfect choice to replace conventional glass fibers as reinforcement in polymer composites [54-57].

In spite of the numerous advantages of NF, their applications are limited. The most important problem is their low interfacial adhesion with most polymeric matrices leading to the reduction of stress transfer from the matrix to the reinforcing fibers [51]. This problem is mainly caused by the relatively high cellulose content of NF and the tendency of water molecules to form the hydrogen bonding with the existing hydroxyl groups on the cellulose structure. Furthermore, moisture absorption in NF leads to dimensional changes of the composites reinforced by NF and, eventually, low interfacial adhesion [58, 59]. To improve fiber/matrix adhesion, many attempts such as physical (e.g. plasma and corona discharge) [60-62], chemical (e.g. silane treatment, acetylation) [63, 64], and physicochemical treatments [65, 66] have been made to modify the surface properties of NF. It should be noted that physical treatment methods can only modify a thin layer of the fiber surface and do not change the hygroscopic characteristics of the fibers [67]. Chemical modification, on the other hand, permanently modifies NF (on the surface and in depth) by replacing the functional hydroxyl groups with suitable functional groups such as amines, methacrylate, epoxides etc… [67]. Chemical modification can be performed by grafting polymers onto the fibers [68, 69], crosslinking the cellulosic chain of fibers [70], and/or using coupling agents [70, 71]. Coupling agents are functional materials that can be used in small quantities to treat a surface to improve the interfacial adhesion. This is only possible when one end of the coupling agent molecule links to the surface of reinforcing materials and the other end reacts with the matrix [72]. Silane compounds have been recognized as one of the most efficient coupling agents which have been extensively employed

in composite materials such as glass fiber reinforced polymer composites [73, 74]. Silanes can be used in NF reinforced polymer composites because NFs carry hydroxyl groups just like the glass fibers [71]. As a result, a proper surface treatment with the silane can normally convert hydrophilic NF into hydrophobic reinforcements for polymeric matrices [67, 75]. In addition, the creation of silane groups hinders the formation of hydrogen bonds between the NFs' microfibrils, leading to a better diffusion of the polymer through the NFs' microfibrils, and facilitates the impregnation of fibers with polymer matrices [76, 77]. Applications of using amino silanes, such as 3-aminopropyltriethoxysilane (APTES) and 3-aminopropyltrimethoxysilane (APTMS), to improve the interface between NF and different polymer matrices (e.g. polypropylene, polylactic acid, and epoxy) are reported in the literature [72]. However, amino-silanes treatment only resulted in a minor reduction of the moisture absorption of NF in comparison with the silanes carrying nonpolar groups like 3-methacryloxypropyltrimethoxysilane (MPTMS) [78]. MPTMS, which is primarily used to make hydrophobic surfaces, is one of the most used coupling agents available for improving the adhesion between polymers and reinforcements [79, 80]. It is well known that silanes' alkoxy groups can directly react with the OH groups in silica thereby forming Si-O-Si bonds [17, 81]. However, the alkoxysilanes cannot directly react with the hydroxyl groups of cellulosic fibers due to the lower reactivity/acidity of cellulosic hydroxyl groups compared to hydroxyl groups of the silica [82]. An optional strategy could be activating the alkoxysilane by hydrolyzing alkoxy groups and forming more reactive silanol groups. As a result, the silanol can interact with the hydroxyl groups of NFs via hydrogen bonding [82]. However, there are many parameters (e.g. temperature, pH, concentration, and type of solution) which affect the silane hydrolysis and make it hard to control [83]. In addition, hydrogen bonds formed between the silanol molecules and hydroxyl groups of NFs do not convert into covalent bindings of Si-O-C at room temperature, so heat treatment (e.g. 110 ºC for 2 h) is required [81, 84, 85]. To avoid the aforementioned additional steps (hydrolysis and curing/dehydration), a methodology is required to increase reactivity/acidity of the OH groups of the fiber's surface. Carboxylic OH groups are significantly more reactive than the alcoholic OH groups due to the presence of the carbonyl group [86]. Thus, carboxylic OH groups, which can be produced by the oxidation of alcoholic OH groups on the NFs' surface, are able to directly react with silane molecules and form covalent bonds as shown in figure 3.1.

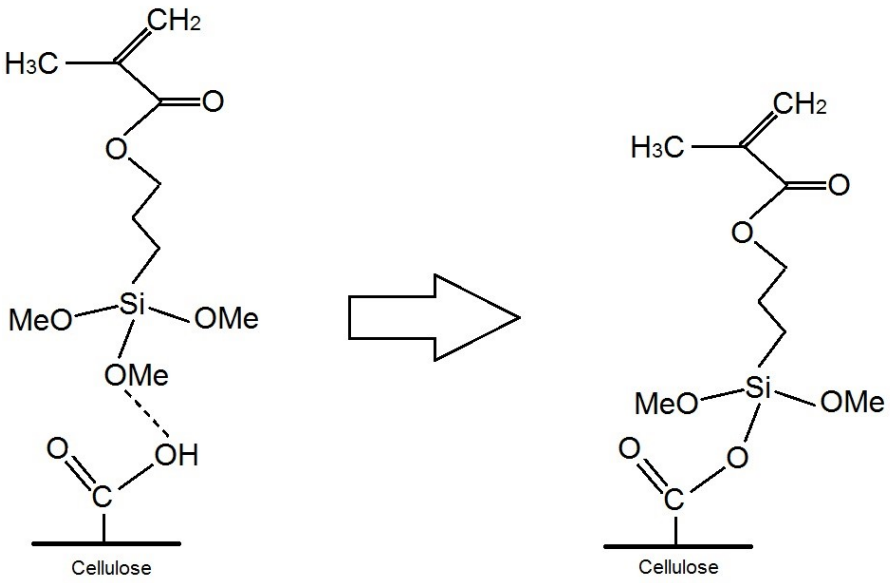

Figure 3.1 Possible mechanism of direct reaction between MPTMS and oxidized Cellulose

Among all the oxidation methodologies, 2,2,6,6- tetramethylpyperidine-1-oxy radical (TEMPO)-mediated oxidation is one of the most interesting modification methods of cellulose. It works under mild aqueous conditions by means of the selective oxidation of primary alcoholic OH groups. Hence, carboxyl functional groups along with a small amount of aldehyde, that is also much more reactive than the alcoholic group, effectively introduce onto the cellulosic fibers [87-90]. Araki et al. used TEMPO oxidation to form carboxyl groups on the microcrystalline celluloses for subsequent coupling of the poly (ethylene glycol) carrying a terminal amino group [91]. Lasseuguette et al. reported successful grafting of the poly (ether-amines) onto the TEMPO-oxidized cellulose [92]. Benkaddour et al. investigated hydrophobization of TEMPO-oxidized cellulose by the coupling of the alkyl ketene dimer (AKD) via esterification. The authors reported an efficient coupling reaction that resulted in a high contact angle (≈ 115 ˚) [93].

The present work first aims to investigate the effect of the TEMPO oxidation on the reactivity of flax fiber surface for the subsequent bonding of the silane coupling agents. It should be noted that oxidation under mild conditions, as well as the minimization of reaction time, are crucial parameters in this work to retaining the mechanical properties of the fiber. Secondly, thermal stability, wettability, and mechanical properties of the surface treated fibers are

analyzed and compared with the as received fiber. Finally, the interaction of the as received and silane treated flax fibers with the bio epoxy resin is studied.

3.4. Experimental

3.4.1. Materials

Flax yarn bobbins were provided by Alysse-creations, France. TEMPO, 3-methacryloxypropyltrimethoxysilane, and Sodium bromide (NaBr) were purchased from Sigma-Aldrich. All other chemicals, such as acetone, methanol, sodium hydroxide (NaOH), hydrogen chloride (HCl), and sodium hypochlorite (NaClO), were provided by Fisher Scientific. The bio epoxy resin (Super Sap CLR) was purchased from Entropy Resins.

3.4.2. Fiber Pre-Treatment

Pre-treatment of flax fibers was performed in three steps. First, flax fibers were treated by boiling acetone under reflux for 45 min to remove waxes, fats, and other impurities (which can weaken the adhesion at the composite interface) from the surface. This was followed by the immersing of dewaxed fibers in a 5 wt. % sodium hydroxide solution for 40 min and immediately rinsing the alkalized fibers with distilled water to neutralize the pH. Eventually, fibers were dried overnight in an air-circulating oven at 50 °C and kept in a desiccator.

3.4.3. TEMPO Oxidation

The TEMPO oxidation was done to carboxylate the existing hydroxyl (primary alcohol) groups on the surface of flax fibers. To do so, 0.13 and 4.7 mmol of TEMPO and NaBr were dissolved in 100 ml of distilled water respectively. Next, 5.65 mmol of NaClO was added to the solution and, after 10-15 min of stirring, the pH was adjusted to 10 ±0.1 by adding some drops of diluted HCl solution to the TEMPO mixture [94]. The TEMPO oxidation took place by immersing flax fibers in the prepared solution. One hundred ml of the TEMPO solution was prepared to oxidize 1 g of pure cellulose (i.e. the flax fibers have approximately 70 wt. % of cellulose in their composition). After immersing the fibers in the solution for 60 seconds [94], they were immediately rinsed with distilled water until neutral pH was reached. Finally, oxidized fibers were dried overnight in the oven at 50 °C and kept in the desiccator for subsequent characterizations.

3.4.4. Silane Treatment

As mentioned before, 3-methacryloxypropyltrimethoxysilane was employed as the coupling agent in this study. Flax fibers were soaked in the neat silane for 30 min at room temperature. The modified fibers were washed with methanol then the fibers were extracted for 16 h with methanol using a Soxhlet apparatus to ascertain the removal of physically bounded Silane molecules as mentioned in the literature review [83, 84]. The treated fibers were dried overnight in the oven at 50 °C and kept in a desiccator before the following characterizations.

3.5. Characterization of the Flax Fiber

3.5.1. Conductometric Titration (Degree of Oxidation)

The concentration of carboxyl groups, in both as received and treated flax fibers, was evaluated by conductometric titration (CT). CT was carried out using a conductivity probe attached to a pH/conductivity meter (Mettler Toledo Seven Multi™). NaOH (0.01 N standard solution) was dispensed from a micro burette into the fiber suspension. To protonate the sodium carboxylate, which formed on the surface of the TEMPO-oxidized fibers, 50 mg of flax fibers were previously immersed in HCl solution (15 mL of 0.01 N standard solution) and were stirred with a magnetic bar for 10-15 minutes [95].

3.5.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR technique was used to determine the functional groups on the surface of flax fibers before and after surface treatments. A total of 64 scans took in the range from 4000 cm^{-1} to 600 cm^{-1} using a JASCO-4600 spectrometer at a resolution of 4 cm^{-1} with an attenuated total reflection (ATR) probe.

3.5.3. X-ray Photoelectron Spectroscopy

Flax fiber surface analysis was performed by an X-ray Photoelectron Spectroscopy to confirm the formation of new functional groups after surface treatments. A KRATOS analytical XPS instrument was used to measure the concentration of the carbon and oxygen on the surface of the as-received and treated flax fibers. For the silane treated fibers, in addition to C and O, the concentration of Si was also measured.

3.5.4. Thermogravimetric Analysis (TGA)

To study the effect of different treatments on the thermal stability of flax fibers and to calculate the amount of the silane on the fiber, a SETARAM thermogravimetric analyzer was used. Samples were heated from the room temperature to 600 ˚C at 10 ˚C/min under an argon flow.

3.5.5. X-ray Fluorescence Spectrometry (XRF)

XRF analysis was performed on a Philips PW2600 Wavelength Dispersive X-ray Fluorescence Spectrometer. Samples were fused to form a lithium borate glass bead at ~1000˚C.

3.5.6. Wettability Test

The wetting angle of fibers in distilled water was obtained by the Wilhelmy method using a Dynamic Contact Angle Tensiometer (DCA-100F). The contact angle can be calculated from the following equation:

$$F = P.\gamma.\cos\theta$$

where F is wetting force (N), γ is the surface tension of the liquid ($N.m^{-1}$), P is the perimeter of the fiber (m), and θ is the contact angle. The fiber diameter was measured by optical microscopy and the average of four measurements along the fiber was calculated. Fibers were placed in the spring loaded clip. A 5 mm immersion depth was selected and the test was conducted at a speed of 0.1 mm/sec. At least five specimens for each sample were tested and the average was reported.

3.5.7. Scanning Electron Microscopy (SEM)

The interfacial adhesion between flax fibers and a bio-epoxy resin before and after the surface treatments was investigated using a Hitachi S-3000N scanning electron microscope under an accelerating voltage of 5 kV. In addition and to observe the silane bonding on the fiber, energy-dispersive X-ray spectroscopy (EDS) was coupled to SEM for elemental analysis. First, a bundle of flax fiber was fixed in the middle of a cylindrical steel mold and then the bio-epoxy resin was poured into the mold. The bio-epoxy based composite rod was cut and polished with the polishing pastes (15, 3 and 1 μm particle size). The preparation process was continued by the sonication (in an ultrasound equipped bath) in the methanol for 1 hr. Finally, the samples were dried and their surfaces were sputter coated with gold/palladium for better imaging.

3.5.8. Tensile test

The tensile test was performed to determine Young's modulus, ultimate tensile strength (UTS) and the elongation at break and also, to confirm that the surface modifications had no adverse effect on the mechanical properties of the as received fibers. All the tensile tests were carried out by applying a Zwick Roell Z050 testing machine equipped with a 100 N load cell according to ASTM D2256. For each condition, at least 30 specimens were tested with a crosshead speed of 200 mm/min and the average values were reported. All samples were dried in an oven overnight at 50 °C and kept in a desiccator before the tensile test. The relative humidity of the environment was 70% and the temperature was 25 ºC during the test. To measure the flax yarn cross-sectional area, almost 20 pieces of flax yarns each 20 mm long, were cut and fixed in a vertical position and then mounted with an epoxy resin. All the samples were cut and polished for observation with SEM. The images were then analyzed to determine the average cross-sectional area. The average was used for calculation of UTS [64].

3.6. Results and Discussion

3.6.1. Degree of Oxidation

Carboxyl concentration has been expressed as the degree of oxidation (DO) according to the equation below:

$$DO = \frac{162 \times V_{NaOH} \times C}{m - V_{NaOH} \times C \times 36}$$

where C is the NaOH concentration (mol/L), V_{NaOH} is the volume of NaOH (L) required to neutralize the carboxylic groups, m is the weight of the dried sample (g), 36 is the difference between the molecular weight of the anhydroglucose unit (AGU) and that of the sodium salt of a glucuronic acid, and 162 is the molecular weight of one AGU [95]. The degree of oxidation showed a significant change (more than 200%) from 3.24e-3 for the non-oxidized sample to 9.74e-3 for the TEMPO-oxidized flax fibers indicating the increment of carboxylic group content due to oxidation.

3.6.2. FTIR Analysis

As mentioned before, to prove the efficiency of the surface modifications on the flax fiber, the fibers were characterized by FTIR. As is shown in Figure 3.2a, the peak around 1730 cm^{-1} corresponding to carbonyl group vibration can be identified. The appearance of the

aforementioned peak, in the as received fibers spectrum, indicates the presence of the hemicelluloses in the fiber structure [96]. After alkaline treatment of the flax fibers, the peak disappears (Figure 3.2b) which indicates the elimination of non-cellulosic (hemicelluloses) compound from the surface of the fiber. In addition, it was found that the O-H/C-H peaks intensity ratio (around 3300 cm-1 and 2900 cm-1, respectively) was increased (by 40%) due to the alkaline treatment. It can be related to the expose of hydroxyl groups through removal of the hydrocarbon rich layer (wax) from the flax fiber`s surface. As previously mentioned, the alkalinized flax fibers cannot directly react with the MPTMS due to low acidity/reactivity of alcoholic OH groups. In fact, a great portion of the physically adsorbed silane molecules on the Alkali-Silane fiber surface can be easily removed after Soxhlet extraction (Figure 3.2c). The reappearance of the peak around 1730 cm-1 (Figure 3.2d) for the oxidized flax fibers confirms the formation of carboxylic acid group (through the protonation of sodium carboxylate ions) on the fibers` surface [92]. The intensity of the aforementioned peak was significantly increased after silane treatment of oxidized fibers (Figure 3.2e). According to the presence of the carbonyl group in the MPTMS structure (Figure 3.3), this increase in the peak intensity can be interpreted as the successful bonding of the MPTMS molecules on oxidized fibers.

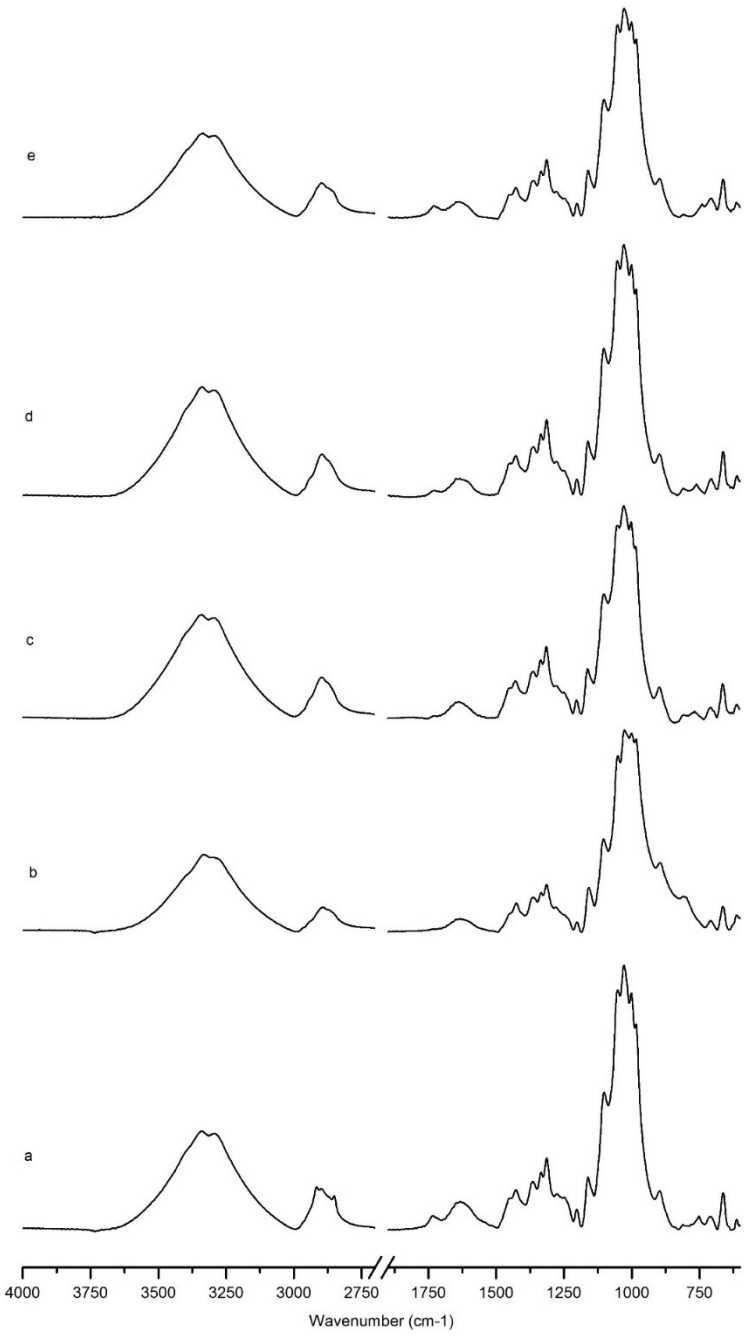

Figure 3.2 FTIR spectrums of as received (a), alkali (b), alkali-silane (c), oxidized (d) and oxidized-silane (e) treated flax fibers

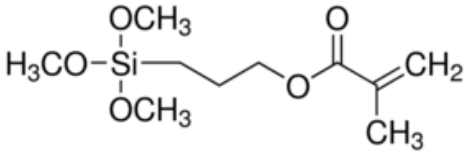

Figure 3.3 Chemical structure of MPTMS

3.6.3. X-ray Photoelectron Spectroscopy

The XPS analysis of flax fibers was conducted to investigate the chemical composition of flax fiber surface with different modification and to compare the silane bonding efficiency of the TEMPO-oxidized and alkaline treated fibers. XPS results for as received, Alkali-Silane and Oxidized-Silane flax fibers are summarized in Table 3.1.

Table 3.1 Elemental Analysis of treated and untreated fibers

	Atomic Concentration (%)			
	O	**C**	**Si**	**O/C**
As Received	30.17	67.95	0.7	0.44
Alkali-Silane	37.4	61.25	0.34	0.61
Oxidized-Silane	32.8	64.35	1.2	0.51

In general, flax fibers contain approximately 70 wt. % cellulose ($C_{12}H_{22}O_{10}$; O/C ≈ 0.83), 18 to 19 wt. % hemicellulose (O/C ≈ 0.83), and 2 to 2.5 wt. % lignin (O/C ≈ 0.35) [97]. Table 1 shows that the O/C ratio for as received flax fibers is around 0.44. This is much lower than the calculated value for a cellulosic surface (O/C ≈ 0.83). It can be concluded that the surface of the as received fibers is mainly covered by hydrocarbon-based wax [97]. The oxygen atomic concentration on the surface of fibers remarkably increased (by 38%) after the alkaline treatment that can be attributed to the removal of hydrocarbon waxes from the surface of flax fibers. Although the probing depth of infrared spectroscopy (micrometers) and XPS (nanometers) are different, this increase in oxygen atomic concentration, after alkaline treatment, is in good agreement with the FTIR results. A small amount of silicon was also detected on the surface of the as received fibers, which was s significantly decreased after alkaline treatment. This can be explained by the presence of silicon-based impurities on the surface of the flax fibers that were removed after pre-treatment. The Si atomic concentration has significantly increased (by 250%) on the Oxidized-Silane fibers` surface in comparison with alkaline-silane treated fibers. This increase can be explained by the effective bonding of MPTMS molecules on the oxidized fiber's surface. In addition, fiber surface O/C ratio dropped from 0.61 to 0.51 due to the carbon-richer silane coverage [84].

3.6.4. Thermal Analysis

The thermogravimetric analysis (TGA) of the as received Alkali-Silane and Oxidized-Silane fibers is depicted in Figure 3.4.

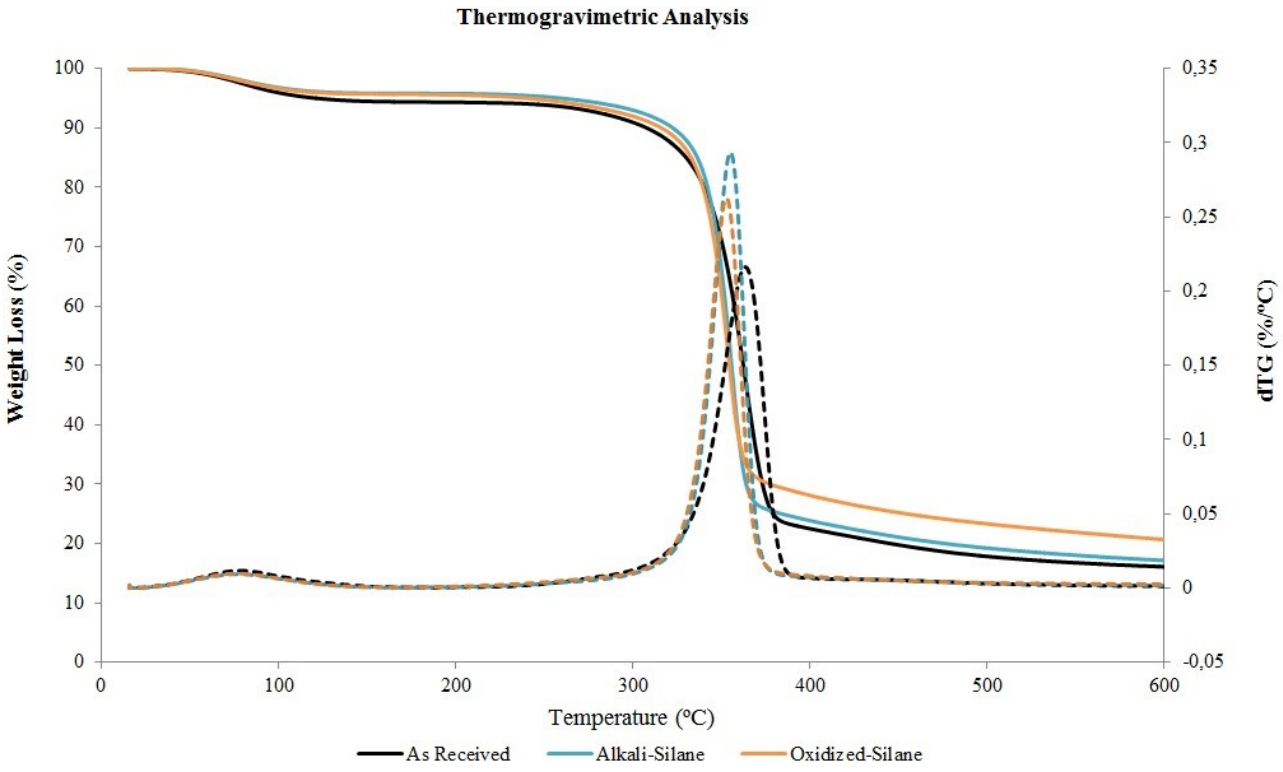

Figure 3.4 Weight loss (solid lines) and Differential thermogravimetric (dash lines) of as received and surface treated fibers

It illustrates the weight loss, the initial degradation temperatures and maximum decomposition temperatures (T_{max}) of fibers. The initial weight loss ranging from 40 to 100 °C is due to the evaporation of the adsorbed water. Both weight loss and differential thermogravimetric (dTG) curves reveal that the decomposition of the fibers mainly started around 260 °C following a sharp weight loss in the range of 340-390°C. In the range of 260-390°C, the cellulose content of the fiber was entirely decomposed due to the breakdown of its molecular structures [96]. The TGA results imply that alkali treatment and tempo oxidation slightly modify the fiber's thermal behavior by decreasing the T_{max} from 360 °C for as received fibers to 358 °C and 355 °C for Alkali-Silane and Oxidized-Silane treated fibers, respectively. This small decrease could be a result of the partial degradation of flax fiber cell walls in alkaline or oxidizing environments [96, 98]. Meanwhile, from the difference of the weight loss (%) under argon

atmosphere between 100–390 ºC, the quantity of grafted silanes onto the surface fibers can be calculated by the following equation:

$$Si_{graft} = W_{100\text{-}390} \times 1000/M$$

Where Si_{graft} is the grafted silanes (mmol/gram of flax fiber), $W_{100\text{-}390}$ is the difference (in decimal number form) of the weight loss between surface treated and as received samples, and M is the molecular mass of the hydrolyzed MPTMS [96]. Results are shown in Table 3.2 and confirm that, despite strong bonding of silane on the oxidized fiber's surface, most of the adsorbed silanes on the alkali fiber's surface are removed after the Soxhlet extraction.

Table 3.2 Calculated grafted Silane through TGA and XRF analysis

Material	**As Received**	**Alkali-Silane**	**Oxidized-Silane**
TGA Analysis			
Si (mmol/$gram_{cellulose}$)	----------	0.04	0.26
XRF Analysis			
SiO_2 (mmol/$gram_{cellulose}$)	0.02	0.034	0.156

To prove the presence of silicon in the decomposed fiber's residue, about 20 grams of as received Alkali-Silane and Oxidized-Silane fibers were heated up to 800 ºC in a furnace. The charring residue was precisely weighted and characterized by XRF to determine the Silicon percentage. The results are presented in Table 2 and are in good agreement with the TGA. Values of bounded silane calculated from XRF, XPS, and TGA results are expected to differ because of the assumptions required. However, the significantly greater silicon concentration on the oxidized fibers over that of alkali treated is consistent when measured by each method.

3.6.5. Wettability Analysis

The results of contact angle measurements are summarized in Table 3.3. It was found that alkaline treatment of flax fibers, even though followed by silane treatment, decreased the contact angle (-22.7o) and significantly increased the flax fiber water absorption (+238%). According to the previous study by Boulos et *al.* after alkaline treatment, the presence of hydroxyl groups on the surface of the flax fibers was increased [99]. This is due to the removal

of non-cellulosic compounds (hemicellulose, lignin) from the fibers, which increased the exposure of cellulose and hence made it more hydrophilic [64, 85].

Table 3.3 Wettability analysis of the flax fibers

	Contact Angle		Water uptake (%)	
	Average	**SD**	**Average**	**SD**
As Received	72.5	3.7	159	14.4
Alkali-Silane	49.8	10.8	378	38.7
Oxidized-Silane	76.5	6.6	168	11.2

These results also confirmed that silane molecules were physically adsorbed on the surface of Alkali-Silane fibers and easily removed after the Soxhlet extraction. In contrast to Alkali-Silane fiber, Oxidized-Silane flax fiber exhibited a significant decrease (≈ 210%) in water absorption and a higher contact angle (+26.7 °) which were close to the results of as received fibers. It can be concluded that the silane molecules reacted with the oxidized fiber surface and reduced the hydrophilicity of the flax fiber due to possessing hydrophobic functional groups.

3.6.6. Scanning Electron Microscopy

The interface between flax fibers (as received and surface treated) and the bio-epoxy resin was shown in Figure 3.5. The gaps between the as received fibers and epoxy resin (Figure 3.5a) clearly demonstrate poor adhesion between the fibers and the resin which is mainly due to the presence of non-cellulosic compounds (such as lignin, hemicellulose, waxes, and other impurities) on the fiber's surface. The observation of micrograph 3.5b shows that the alkaline treatment followed by the silane treatment partially improved the interfacial adhesion between fiber and polymer matrix. Since a major portion of silane molecules was removed by Soxhlet extraction, this improvement can be related to the elimination of non-cellulosic compounds and impurities, such as waxes, by alkaline treatment [100].

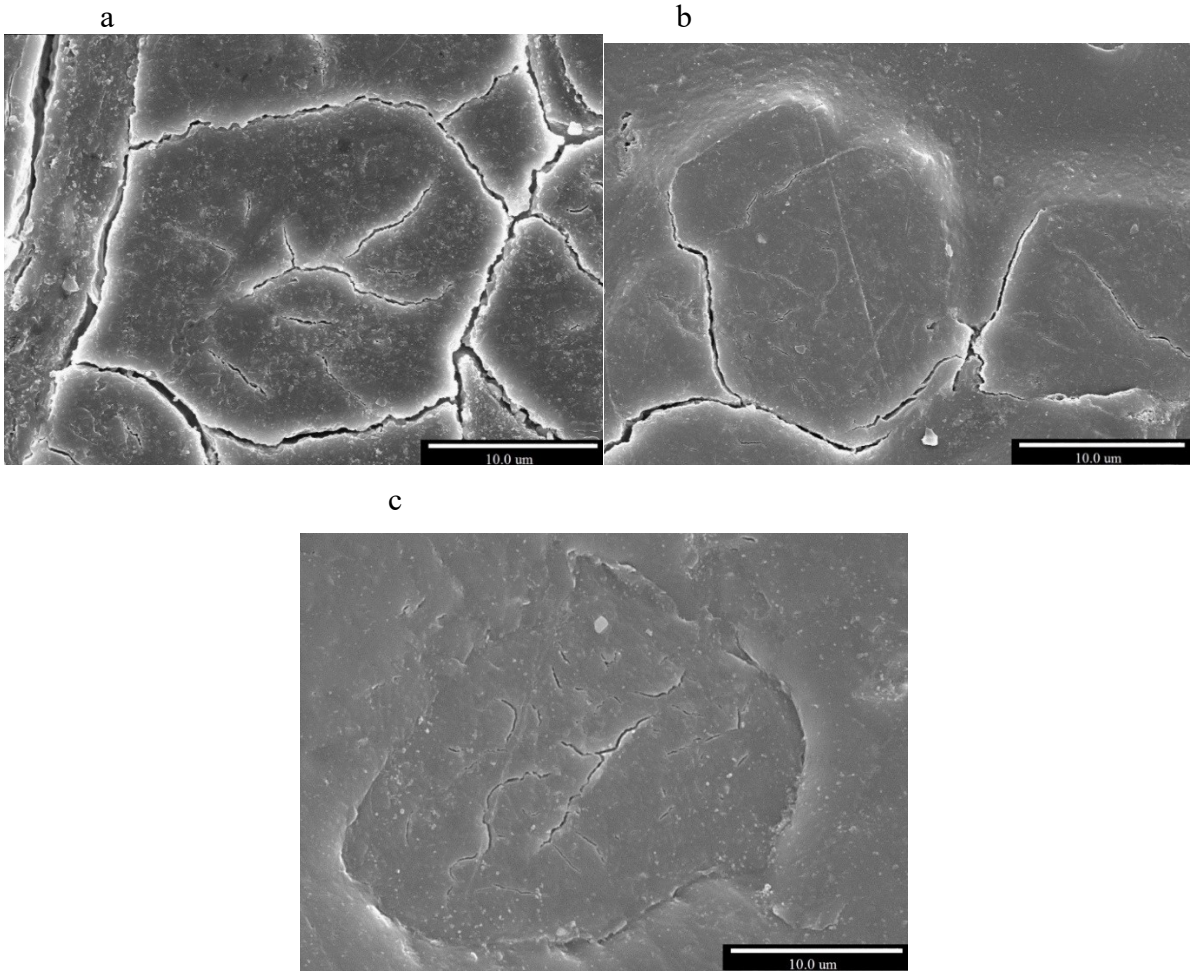

Figure 3.5 SEM micrographs of fiber/matrix interface for a) as received, b) Alkali-Silane treated and c) Oxidized-Silane treated flax fibers

It can be observed in Figure 3.5c that the interface between Oxidized-Silane fibers and epoxy resin is noticeably improved due to a proper interaction between functional groups of flax fibers and epoxy matrix. Figure 3.6 demonstrates the presence of grafted silane (red dots) on the surface of the flax fiber via the EDS mapping. The micrograph of Figure 3.6b shows that silane molecules are entirely grafted to the surface of the Oxidized-silane fiber whereas only a negligible amount of silane molecules are bonded to the Alkali-Silane fibers (Figure 3.6a). However, it seems that the distribution of bonded silanes is not homogeneous. It can be related to the fact that flax fibers were modified by TEMPO oxidation in a heterogeneous system for 60 seconds, thus, oxidizing agents cannot thoroughly diffuse across the fiber to modify alcoholic groups underneath the surface.

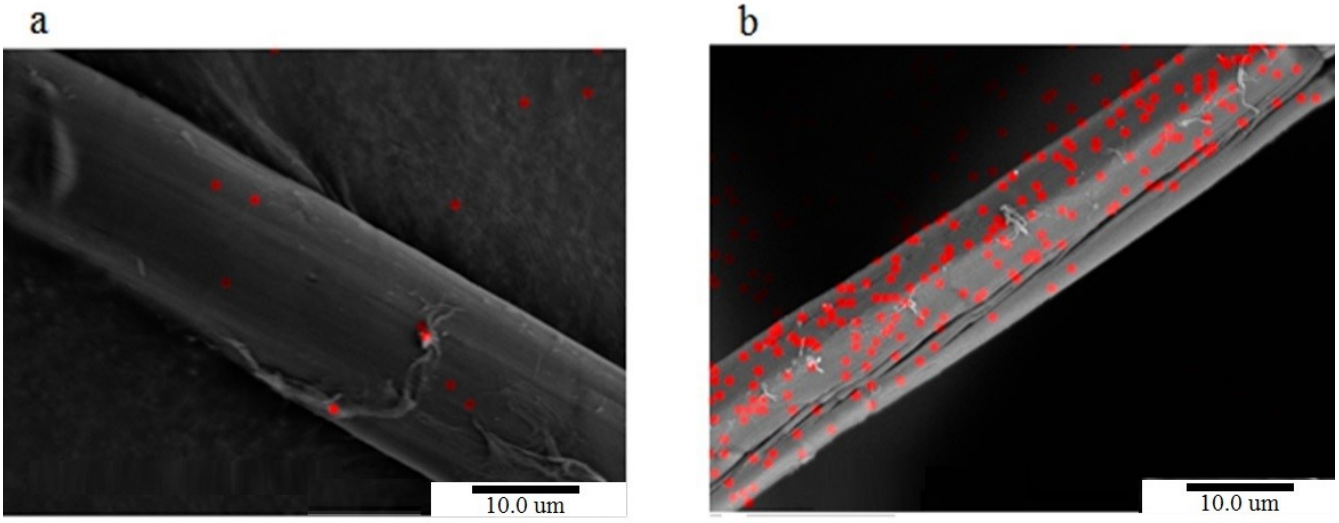

Figure 3.6 SEM/ EDS micrographs of Alkali-Silane fiber (a) and Oxidized-Silane fiber (b)

The EDS method also gives the information from a couple of microns beneath the surface. Thus, distribution of the silane molecules seems to be not homogenous. The SEM analysis results are in good agreement with the thermogravimetric analysis and the fiber's wettability results as previously discussed.

3.6.7. Tensile Properties

The mechanical properties of as received, alkali and oxidized treated flax yarns, before and after silane treatment, are listed in Table 3.4. The relative Stress-Strain curves are shown in Figure 3.7. It was found that Young's modulus (E) of the flax yarns was decreased (≈ 14%) after alkaline treatment whereas the UTS and the strain (elongation at break) were increased by 20% and 23% respectively. The alkali treatment removed non-cellulosic ingredients of the flax fibers (such as hemicellulose, pectin, lignin, etc…) which led to interfibrillar matrix softening [101]. Subsequently, the release of the initial strains can help the cellulose chains to rearrange themselves in a more compact orientation [101]. Thus, an improvement in fiber strength can be obtained using alkali treatment [102, 103]. Moreover, the silane treatment of alkali treated fiber was not successful and had no tangible effect on the mechanical properties of the fiber.

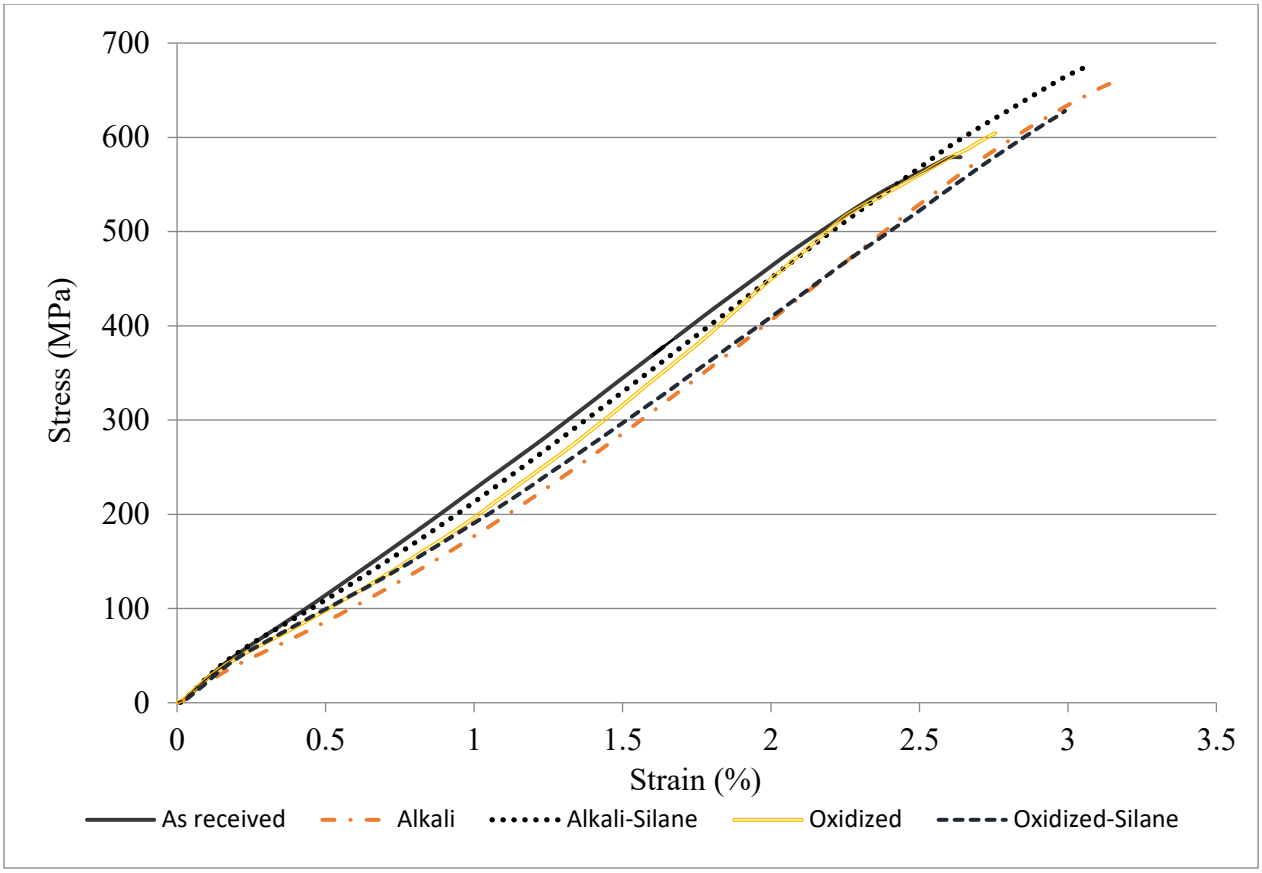

Figure 3.7 Stress-Strain curves of the as received and surface treated flax yarns

Table 3.4 Average values and standard deviations (SD) of the mechanical properties of the fibers

		E (GPa)	SD	UTS (MPa)	SD	ε_H (%)	SD
As Received (Y_1)		30.6	4.15	557	55.2	2.6	0.25
Alkali (Y_2)		26.4	4	667	30.1	3.2	0.33
Alkali-Silane (Y_3)		25.1	4.7	682	52.4	3.3	0.32
Oxidized (Y_4)		24.2	4.2	602	56.5	2.8	0.3
Oxidized-Silane (Y_5)		28.3	3	621	58	3.0	0.3
Y_1, Y_2	Difference (%)	13.7		19.7		23	
	P-Value	<< 0.05		<< 0.05		<< 0.05	
	Difference (%)	18		22.4		27	

Y_1, Y_3	P-Value	<< 0.05	<< 0.05	<< 0.05
Y_1, Y_4	Difference (%)	21	8	7.7
	P-Value	<< 0.05	< 0.05	< 0.05
Y_1, Y_5	Difference (%)	7.5	11.4	15.4
	P-Value	< 0.05	< 0.05	<< 0.05
Y_2, Y_3	Difference (%)	5	2.2	3.1
	P-Value	> 0.05	> 0.05	> 0.05
Y_4, Y_5	Difference (%)	14.5	3.1	7.1
	P-Value	<< 0.05	> 0.05	< 0.05

The Young's modulus and UTS of the flax fibers were slightly decreased after the TEMPO oxidation in comparison to alkali treated fibers (≈ 8 and 10%, respectively). This reduction is primarily related to the dissolution of non-cellulosic ingredients that led to the interfibrillar matrix softening of the flax fibers. However, the oxidized fibers still showed higher UTS in comparison to the as received fibers. The Young's modulus of the oxidized fiber was improved after silane treatment. Again, it can be related to the bonding of silane molecules which can reduce the stress concentration at the surface defects by means of blunting the crack tips [104]. In order to evaluate the average values of the tensile properties, a statistical analysis (t-test) was carried out to confirm that the obtained tensile properties were statistically significant. A desired 95% confidence level (P-value < 0.05) was considered which indicates that the dissimilarity among the mechanical properties is statistically reliable [64].

3.7. Conclusion

In this study, the flax yarns were modified by TEMPO oxidation to convert primary hydroxyl groups into more reactive carboxyl groups. Then, in contrast to conventional silane treatment, the 3-methacryloxypropyltrimethoxysilane was directly applied on the surface of the flax fibers without pre-hydrolysis and dehydration. According to the experimental results, it is concluded that:

• TEMPO oxidation significantly increased the reactivity of the flax fiber surface. This reactivity improvement led to an efficient bonding of the silane coupling agent without any need for pre-hydrolysis and curing/dehydration.

• The bonding of 3-methacryloxypropyltrimethoxysilane on flax fibers increased the contact angle (with water) of the flax fibers. In addition, water absorption significantly decreased in the Oxidized-Silane fibers.

• Fiber/matrix adhesion was slightly improved after the alkaline treatment of flax fibers whereas Oxidized-Silane fibers demonstrated a good adhesion with the bio-epoxy resin.

• Mechanical properties of Oxidized-Silane fibers were improved in comparison to as received fibers although the UTS was lower than the alkali treated fibers due to the partial degradation of microfibrils.

Finally, it was hypothesized that TEMPO oxidation can pave the way for the direct bonding of the MPTMS coupling agent on the surface of flax fiber. Subsequently, the bonded MPTMS molecules decreased the hydrophilicity of flax fiber by means of partial replacement of cellulosic alcohol groups with methacrylate groups. This surface modification significantly improved compatibility between the flax fibers and the bio-epoxy resin.

4. Efficient one step silane treatment of flax fibers through TEMPO oxidation to improve the interfacial adhesion in flax/bio epoxy composites

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4.1. Résumé

Les fibres naturelles sont reconnues comme étant une excellente alternative aux renforts traditionnels dans les composites polymères. Cependant, le principal inconvénient des fibres naturelles est leur faible interaction avec les matrices polymères en raison de leur nature hydrophile. Afin d'améliorer leur compatibilité dans les composites, des traitements de surface sont nécessaires. Le traitement au silane a été largement utilisé pour modifier le caractère hygroscopique des fibres naturelles. Dans cette étude, une nouvelle méthode de traitement au silane sans pré-hydrolyse ni durcissement/déshydratation des groupes silanol a été développée. Pour ce faire, les fibres de lin ont été modifiées par oxydation TEMPO suivie d'une application directe de l'aminosilane. L'adhérence interfaciale fibre/matrice a été examinée en mesurant la résistance au cisaillement interlaminaire. Des analyses thermogravimétrique (TGA) et mécanique dynamique (DMA) ont été effectuées pour étudier la résistance thermique et les propriétés thermomécaniques des composites. Les résultats ont révélé que l'adhésion fibre/matrice a été améliorée dans le composite avec fibres silanisées oxydées. De plus, l'absorption d'eau a été significativement réduite (20%) dans le composite renforcé de fibres silanisées oxydées par rapport au composite d'origine.

Mot-clé : Fibre lignocellulosique, Liaison Fibre/Matrice, Traitements de surface, Oxydation TEMPO.

4.2. Abstract

Natural fibers have been approved as an excellent alternative for traditional reinforcements in polymer composites. However, the main disadvantage of natural fibers as reinforcements is their poor interaction with polymeric matrices due to their hydrophilic nature. In order to improve their compatibility as composite reinforcement, surface treatments are required. Silane treatment has been widely used to modify hygroscopic properties of natural fibers. In this study, a new method of silane treatment has been developed without the pre-hydrolysis and curing/dehydration of silanol groups. To do so, flax fibers were modified through TEMPO mediated oxidation followed by direct application of the amino-silane. The fiber/matrix interfacial adhesion was examined by measuring inter-laminar shear strength. Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA) were performed to study the thermal resistance and thermo-mechanical properties of the composites. The results revealed that fiber/matrix adhesion was improved in the oxidized silanized fiber composite. In addition, water absorption was significantly reduced (20%) in the oxidized silanized fiber reinforced composite compared with the as received one.

Keyword: Lignocellulosic fiber, Fiber/Matrix bonding, Surface treatments, TEMPO oxidation

4.3. Introduction

Fiber reinforced polymer composites are widely used in the construction, transport, and automotive industries to replace conventional industrial materials due to their high specific mechanical properties e.g. strength and modulus. However, there are some concerns in the application of polymer composites like the non-renewable petroleum resources in the world and the environmental problems that are caused by the end of life (EOL) of polymeric products [105]. Unfortunately, most of the petroleum based polymers are not biodegradable or compostable and their recycling processes are not as straightforward as for metallic products. Given the aforementioned problems, there is a great interest in the manufacturing of ecofriendly, green and biodegradable polymer composite materials from renewable resources. Natural fibers are relatively cheap, lower in density, biodegradable, and renewable materials that demonstrate good mechanical properties. Therefore, the demand for using them as a glass fibers replacement in composites is continuously growing [53]. The world consumption of natural fibers in 2010 amounted to 315 kilotons (13% of the total reinforcement materials) and it is forecasted that 830 kilotons of natural fibers will be utilized by the year 2020 (28% of the total reinforcement materials) [106]. Flax fiber is one of the most used natural fibers due to its specific strength properties that make it comparable to glass fibers. They can be employed in the secondary structural applications such as automotive interior panels, package trays, partition walls, and furniture [107]. Canada is the largest producer of flax in the world and produced over 500 kilotons of flaxseed in 2017 [108] which was mostly exported to China, Belgium and USA. Since flax straws are considered as residues, utilization of flax fibers as reinforcement in polymer composites would be an opportunity to valorize this biomass into added value bio-products. However, similar to other natural fibers, the main drawback of flax fibers is their hydrophilic nature (due to the presence of hydroxyl groups in their structure) and thus, the tendency of water molecules to absorb into the fiber structure [109]. Moisture absorption of flax fibers leads to the dimensional change of the fiber and eventually weakens the interfacial adhesion at the composites interface [110]. In addition, the hydrophilic nature of flax fiber makes it incompatible with polymeric matrices that are mostly hydrophobic. To overcome these disadvantages, various surface treatments (e.g. Alkaline, Maleic Anhydride, Silanes etc...) are proposed

to modify the surface and/or bulk properties of flax fibers. Alkaline treatment is one of the simplest methods to eliminate the impurities from the surface of the natural cellulosic fibers in order to activate/exposed functional groups on fibers. An appropriate amount of sodium hydroxide (NaOH) removes undesired ingredients (e.g. lignin, hemicellulose) from the natural fibers' surface and facilitates subsequent modifications like silane treatment and/or polymer grafting [111]. Sepe et al. studied the effect of alkaline and silane treatment on the mechanical properties of hemp/epoxy composites. Their results revealed that alkaline treatment followed by the application of (3-Glycidyloxypropyl) trimethoxysilane can enhance the mechanical properties of the composite [112]. In another study, Lu et al. examined the effect of similar treatments on the mechanical performance of bamboo fiber/epoxy resin composite. They found that alkaline and silane treatment increased tensile strength and elongation at break but slightly decreased impact strength [113]. Georgiopoulos et al. reported that surface treatment of flax fibers with maleic anhydride resulted in the highest Young's modulus increment in flax/PLA composite. In contrast, vinyltriethoxy silane slightly improved tensile strength and reduced all flexural properties of the composite [114]. Alix et al. examined the effect of various chemical treatments (maleic anhydride, acetic anhydride, methacryloxy propyl trimethoxy silane and styrene) on the mechanical properties of flax fibers. They found that only silane treatment enhanced the tensile modulus and strength of flax fiber while other chemicals reduced the fiber's mechanical properties [115]. Mokhothu and John applied bio-based coatings (poly furfuryl alcohol, polyurethane and a commercial resin) on flax fibers and investigated the hygroscopic and mechanical properties of flax fiber/phenolic resin composite. They found that poly furfuryl alcohol coated fiber reinforced composite exhibited higher moisture resistance and mechanical properties after long term conditioning/aging [116]. Bayart et al. used a nano reinforced epoxy coating on flax fibers, which improved inter-laminar shear strength and reduced water absorption of the flax/PLA (poly lactic acid) composite [117]. Kabir et al. showed that hemp fibers treated with acetic anhydride and oligomeric siloxane deteriorate the fibers' mechanical properties. They demonstrated that alkaline treatment of fibers slightly increased mechanical properties of silane treated hemp fibers but did not exceed as received fibers` mechanical properties [118].

As reviewed above, trialkoxysilane treatment, initially developed for functionalization of glass fibers [16], is widely used for the modification of natural fibers. Natural fibers (e.g. flax, hemp, bamboo) have hydroxyl groups on their surface like glass fibers. Thus, silane coupling agents can react with hydroxyl groups and alter the surface properties of natural fibers to make them more compatible with polymeric matrices. In addition, silanes can hinder the formation of internal hydrogen bonding between cellulosic molecular chains that leads to better diffusion of polymer resins and consequently higher impregnation of fibers. However, because of the lower reactivity/acidity of hydroxyl groups of natural fibers in comparison to glass fibers, they cannot directly react with trialkoxysilanes. They should be pre-hydrolyzed in specific pH to form more active silanol groups; then, interact with hydroxyl groups on the fibers` surface via hydrogen bonding. Also, a heat treatment at elevated temperature (110-120 °C) is required to transform the hydrogen bonding between silane molecules and fibers into the covalent bonding [15]. The improvement of reactivity/acidity of OH groups on the fiber's surface would be an option to eliminate those additional steps (pre-hydrolysis and heat treatment). Carboxylic OH groups are significantly more reactive than the alcoholic OH groups due to the presence of an adjacent carbonyl group [18]. Thus, by oxidation of alcoholic OH groups of flax fibers to carboxylic groups, silane molecules might directly react with flax fibers and form covalent bonds. An interesting oxidation method for cellulosic fibers is 2,2,6,6-tetramethylpyperidine-1-oxy radical (TEMPO) mediated oxidation. TEMPO mediated oxidation selectively oxidizes primary alcoholic OH groups which results in the introducing of carboxyl functional groups along with small amount of aldehyde onto the cellulosic fibers. It also works under mild conditions (pH ≈ 10) that is crucial to retain the maximum mechanical properties of the fiber [19]. Foruzanmehr et al. compared the grafting efficiency of a titanium dioxide (TiO2) coating between the as received and TEMPO oxidized flax fibers and examined its effect on the final properties of flax/epoxy composite. According to their findings, oxidized flax fibers showed higher interaction with TiO2 coating compared with as received fibers that resulted in higher ILSS and stiffness [119]. Sbiai and coworkers reported significant improvement in flexural properties of the date palm leaf fiber reinforced epoxy composites through the TEMPO oxidation of fibers [120]. As previously reported, non-hydrolyzed silane molecules were

successfully bonded to the TEMPO oxidized flax fiber due to the enhanced reactivity of OH groups on the oxidized fiber`s surface [121]. The silane treated oxidized flax fibers exhibited superior mechanical properties and compatibility with polymer matrix compared to the as received flax fibers. This study aimed to investigate the effect of the non-hydrolyzed silane treatment of flax fibers on the interfacial adhesion, mechanical, and thermal properties of the flax/bio epoxy composite. In addition, water absorption of the as received and silane treated flax/bio epoxy composite were compared.

4.4. Material and Methods

4.4.1. Material

An Entropy Resins' bio epoxy system (Super Sap CLR resin & CLH hardener) was chosen as the matrix to manufacture the composite material. Unidirectional (UD) flax fabric (250 g/m^2) has been supplied by FRD (Fibers Recherche Développement), France. Sodium bromide (NaBr), 3-aminopropyltrimethoxysilane (APTMS) and TEMPO purchased from Sigma Aldrich. Fisher Scientific provided all other chemicals including acetone, methanol, hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium hypochlorite (NaClO).

4.4.2. Sample Preparation

4.4.2.1. Surface treatment

Surface treatment of flax fabric was performed in three main steps. First, flax fabric was immersed in boiling acetone under reflux for 45 minutes to remove fats and other pollutants from the surface of the fibers. Then, alkaline treatment of the fabric was performed in a 5 wt. % sodium hydroxide aqueous solution for 40 minutes at room temperature. Alkaline treated fabric was rinsed with distilled water to adjust the pH of fibers to 7. In the second step, alkaline treated fabric was oxidized in the TEMPO mediate solution to transform primary alcoholic (OH) groups to sodium carboxylate functional groups as previously described [121]. Sodium carboxylate groups were subsequently converted to carboxylic acid groups via protonation in diluted hydrochloric acid. Finally, non-hydrolyzied APTMS was sprayed on the oxidized flax fabrics and kept for 30 minutes at room temperature. Then, silane treated fabrics were rinsed with

methanol several times to ascertain the removal of physically absorbed silane molecules. The treated fabrics were dried overnight in the oven at 60 °C and stored in a desiccator before further processing.

To prove the role of TEMPO mediated oxidation in silane modification of flax fibers, alkaline treated flax fabrics were also immersed in a silane solution for 30 minutes. The silane solution was prepared by the addition of 3% wt. of APTMS (by weight of the fabric) into the 80:20 methanol/water mixture. The pH of the mixture was adjusted to ≈ 4 and mixture was stirred for 15 minutes before the immersion of flax fabrics [121]. Silane treated fabrics were dried overnight in the oven at 60 °C and stored in a desiccator. Abbreviations for as received and surface treated fabrics are shown in Table 4.1.

Table 4.1 Abbreviations of flax fabrics with different surface treatments

Abbreviation	Description
As Rec	As Received fabrics
Alk-APS	Pre-hydrolyzed Silane treatment
Ox-APS	TEMPO oxidation followed by Silane treatment (without pre-hydrolysis)

4.4.2.2. Composite manufacturing

Flax/bio epoxy composite sheets were fabricated (as received and surface treated flax fabrics) through the compression molding process. The bio epoxy resin was properly mixed with the hardener (Super Sap CLH) in 2:1 volumetric ratio. Four layers of impregnated UD flax fabric were hand lay-up within a metallic frame, then covered by Teflon sheets and pressed under around one metric ton pressure at 40°C for approximately 2 hours.

4.5. Characterization

4.5.1. Thermogravimetric analysis

To prove that TEMPO mediated oxidation of flax fibers did not adversely affect thermal properties of the composite, as received and surface treated flax/epoxy composites were examined by means of a SETARAM thermogravimetric analyzer (TGA). Samples with

masses in the range of 20-25 mg were heated, under Argon atmosphere, from room temperature up to 600 ˚C at the heating rate of 10 ˚C/min.

4.5.2. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is a sensitive method for studying changes in the mobility of polymeric molecular chains including transitions and relaxations; thus, it is able to assess the effect of different modifications (on the fiber, matrix and interface) in composite materials [122]. As received and surface modified- fiber reinforced epoxy composites were characterized by dynamical mechanical analysis (DMA 8000, PerkinElmer) in the single cantilever mode. The glass transition temperature (T_g) of composites is determined based on the intersection of two tangent lines from the storage modulus (E') curve according to ASTM D7028 [123]. The specimens were heated up from 25 to 120 °C at 1 Hz frequency with a heating rate of 3°C/min. At least three specimens were tested for each condition.

4.5.3. Inter-Laminar Shear Strength (ILSS)

The Short Beam Shear (SBS) test of a unidirectional composite is carried out to measure the interfacial bond strength between the fiber and matrix. The SBS test was conducted on a table top (Zwick/Roell Z050) universal testing machine equipped with a 30 kN load cell in three-point bending mode. The crosshead speed was 1 mm/min and the span-to-thickness ratio was set at 4 [124]. At least five samples for each condition were characterized and the average was reported.

4.5.4. Three point bending test

To determine the effect of surface modifications on the flexural properties of flax/bio epoxy composites, the three point bending test was performed using a table top (Zwick/Roell Z050) universal testing machine equipped with a 30 kN load cell. Composite specimens were cut in a length to thickness ratio (L/D) equal to 32 while tests were conducted with a crosshead speed of 1.5 mm/min according to ASTM D790 [125].

4.5.5. Scanning Electron Microscopy (SEM)

SEM analysis was carried out by means of a Hitachi S-3000N at 3 kV to observe the cross sections of the flax fiber reinforced bio epoxy resin to determine the quality of the fiber

matrix adhesion. The fractured surface was prepared by immersing of the composite specimen into liquid nitrogen bath followed by breaking them by hand. Then, specimens were coated with a thin layer of gold–palladium by vapor deposit process before SEM analysis.

4.5.6. Water Absorption

Water uptake measurements were performed by immersing the composite specimens in distilled water at 25 °C. Composite specimens were periodically removed from water, the excess water was wiped with the tissue and weighed immediately according to ASTM D 570 [55]. Water uptake was calculated using below equation:

$$M = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100$$

where M is the mass gain due to the water uptake where M_{dry} and M_{wet} are the masses of the specimens before and after immersion, respectively. Water penetration into the polymer composites is conducted by three different mechanisms:

a) By diffusion between polymer molecular chains.
b) By capillarity through the gaps and defects at the composite interfaces
c) By transportation through micro pores and cracks in the matrix that formed during composite manufacturing

Moreover, water can penetrate inside the flax fiber itself that is particularly possible for composite reinforced with twisted fiber yarn [126]. The water absorption of natural fiber reinforced polymer composites linearly increases with the square root of time, according to the Fick`s law. However, rate of absorption gradually decreases when the saturation point is reached. The diffusion coefficient D is calculated from Equation:

$$D = \frac{\pi}{(4M_\infty)^2}\left(\frac{M_t h}{\sqrt{t}}\right)^2 = \pi\left(\frac{k}{4M_\infty}\right)^2$$

where M_t is water uptake at the time t, $M\infty$ is the water uptake at saturation, h is the specimen thickness and k is the slope of the linear part of the curve $M = f(\sqrt{t}/h)$ [126].

4.6. Results and Discussion

4.6.1. Thermogravimetric analysis

The thermogravimetric analysis of the as received, Alk-APS and Ox-APS treated flax fiber reinforced polymer composites is exhibited in Figure 4.1. All samples show an initial weight loss ranging from 80 to 250°C that would be related to the evaporation of the adsorbed water molecules and low molecular weight content of bio epoxy matrix. The second weight loss gradually starts in 250°C that lead to the sharp fall at 330-400°C. This would be corresponded to the degradation of the holocellulose content of flax fibers which, also are overlapped with bio epoxy resin degradation.

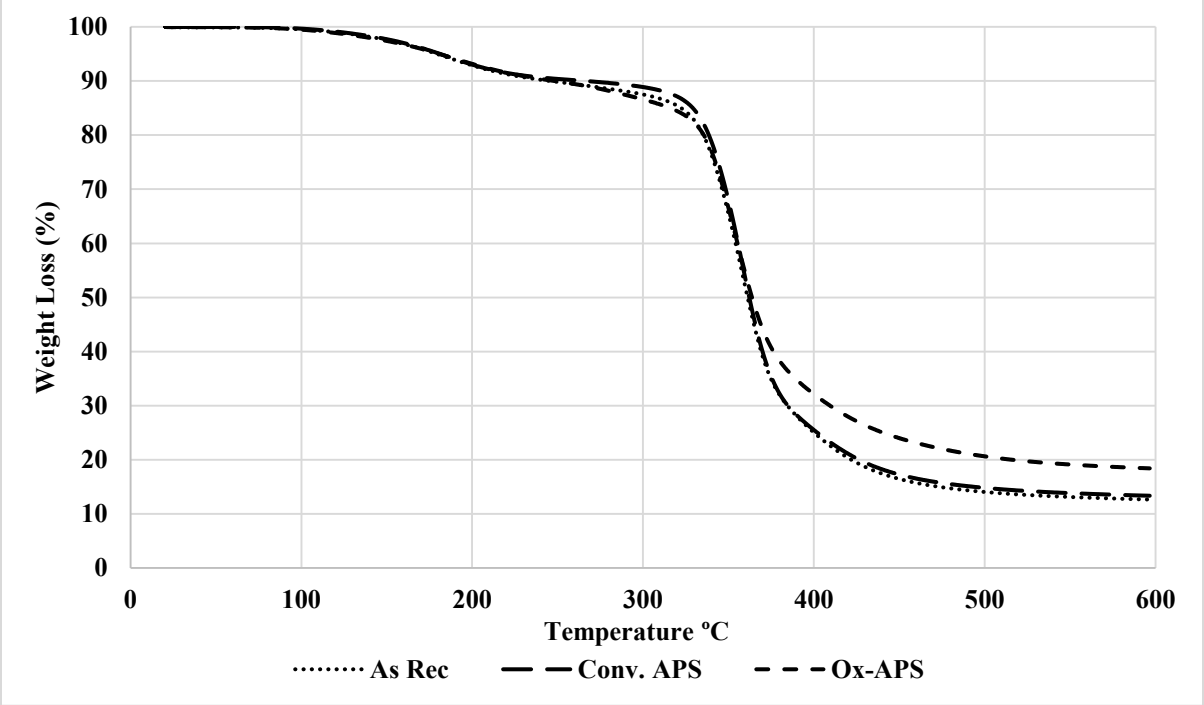

Figure 4.1 Thermogravimetric analysis of as received and silane treated composites

Above 360°C, Ox-APS treated flax showed lower weight loss in comparison to as received and Alk-APS treated fiber composite. It can be interpreted to higher amount of grafted silane molecules on the Ox-APS fibers that was previously confirmed by authors [121]. The maximum decomposition temperature of Ox-APS composite was slightly decreased (from 358ºC to 354ºC) compared to other ones. The results showed that TEMPO oxidation of flax fibers was not adversely affected thermal behaviour of flax/bio epoxy composite.

4.6.2. Dynamic Mechanical Analysis

The results of the dynamic mechanical analysis for the as received and silane treated flax fiber/epoxy composites are shown in Figure 4.2 and Table 4.2. According to diagrams, introduction of flax fibers significantly increased the storage modulus of the bio epoxy matrix at the room temperature. Alk-APS treatment of fibers resulted in a negligible decrease (≈ 5%) in the storage modulus of the composite that might be due to the partial degradation of the fiber during alkaline treatment [127].

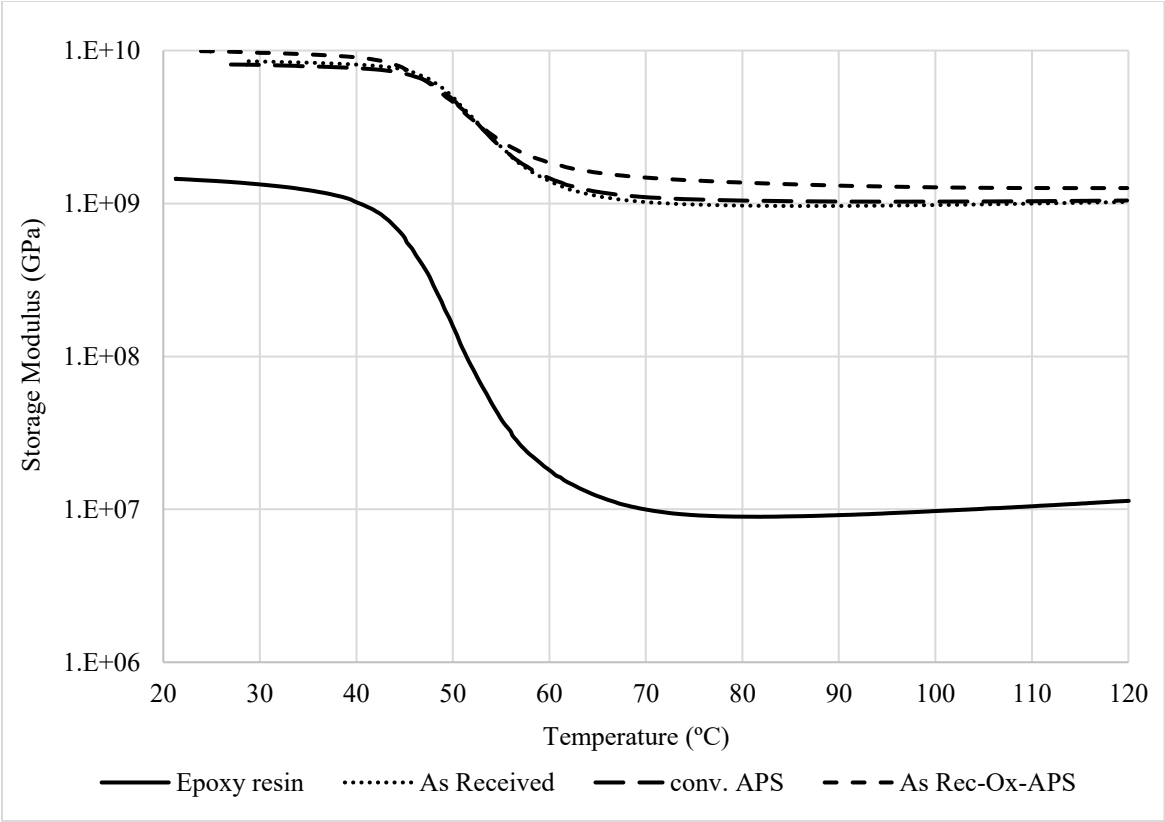

Figure 4.2 Storage modulus of bio epoxy resin and flax fiber reinforced composites

However, the storage modulus improved (≈ 20%) in the Ox-APS treated fiber composites compared to the Alk-APS fibers. This improvement could be attributed to strong adhesion between Ox-APS fibers and bio epoxy matrix and consequently higher load transfer from matrix to fibers [114].

Table 4.2 Dynamic mechanical thermal analysis of as received and silane treated composites

Material	E` (GPa)	C factor	dE'/dT	T_g (°C)	Tan δ at peak
Epoxy resin	1.33	---	---	39	1.03
As Received	8.47	0.078	0.414	45	0.47
Alk-APS	8.05	0.069	0.385	45	0.42
Ox-APS	9.65	0.06	0.428	43	0.35

As demonstrated in Table 4.2, T_g of the composite did not changed after Alk-APS treatment but slightly decreased to 43 °C in the Ox-APS fiber composites. This reduction in T_g might be caused by the grafted amino silane on the fiber surface that improved the interaction with the matrix but formed an interphase with low cross-link density [122, 128]. Jensen et al. simulated a silane modified interphase and observed that the T_g of the crosslinked amino silane network was noticeably lower than neat epoxy resin [129]. They concluded that it would be related to the formation of an interpenetrating network (IPN) of amino silane and epoxy resin at the composite interface. The maximum loss factor (at the Tan δ curve's peak) of composites was also decreased about 10% & 25% in Alk-APS and Ox-APS composites, respectively, in comparison to the as received fiber composite. It can be related to the improved interfacial adhesion after silane treatment of flax fibers [124], however, oxidized flax fibers showed higher improvement due to the more effective silane treatment [130]. The storage modulus values of all composites are sharply dropped at the temperature range of 40-70 °C. Ray et al. found that the slope of this fall (dE'/dT) has an inverse relationship with the defect concentration of the composite (the total amount of defects in the fibers, the fiber/matrix interface and the resin) [131]. According to the results, the defect concentration of composites, increased after conventional silane modification but decreased in oxidized silane treated fiber composite. In addition, the performance of the composites in the glass transition region and the effectiveness of the reinforcement in the composite material can be expressed by the C factor:

$$C = \frac{\left(E'_g / E'_r\right)_{Composite}}{\left(E'_g / E'_r\right)_{Matrix}}$$

where E'_g and E'_r are the storage modulus values in the glassy region (about 40°C) and rubbery plateau (about 70°C), respectively [132, 133]. The extent of the drop in storage modulus (at the temperature range of 40-70 °C) for Ox-APS fiber composite is smaller than as received and Alk-APS fiber composites. It results in lower C value which indicate higher reinforcing efficiency of Ox-APS fibers compared to as received and Alk-APS fibers [132]. These results are in agreement with other analyses and confirm the higher efficiency of silane treatment by means of TEMPO oxidation of flax fibers surface.

Changes in the viscoelastic characteristics of crosslinked polymers after the introduction of reinforcements into the matrix can be also expressed by the Cole-Cole plot [134]. This method was originally developed for the study of dielectric dispersion by means of plotting E" against E' [135]. It can be used to evaluate the homogeneity of reinforced polymers where homogeneous polymeric systems are reported to show a semi-circle diagram [122]. Cole-Cole plot is used to fit the experimental data to a model that relate the dynamic elastic modulus to the unrelaxed modulus (Eu), relaxed modulus (Er) and relaxation times [136]. This model can be used to study how the composite interface influence relaxation processes (described by a distribution of relaxation times). The relaxation processes originated from the tendency of polymer chains to reach the lower energy conformations by means of rearrangement. By introduction of reinforcements into the matrix, the polymer chains mobility restricted by the physical entanglement and/or chemical interaction at the interface. A simplified equation was derived to model polymers during viscoelastic transitions using two relaxation times [122, 137]:

$$E^* = E_r + \frac{E_u - E_r}{1 + (iw\tau_1)^{-h} + (iw\tau_2)^{-k}}$$

where E*= complex modulus; Er = relaxed modulus; Eu = unrelaxed modulus; τ_1 and τ_2 = relaxation times; w = frequency; h = long time parameter; k = short time parameter. The Er and Eu are determined by extrapolating the Cole-Cole plot that are close to the value of storage modulus in rubbery and glassy region, respectively. Moreover, parameters (h) and (k)

are calculated from angles that made by extrapolated curve and the E' axis as defined in Figure 4.3.

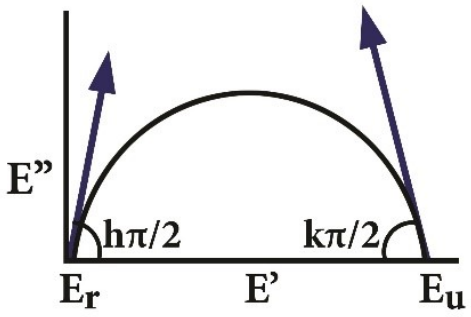

Figure 4.3 Illustration of extrapolated angles in Cole-Cole plot

Parameters h and k are related to any heterogeneity in the polymer that can disturb the relaxation processes like the composite interface. The Cole-Cole plot derived data are illustrated in Table 4.3.

Table 4.3 Cole-Cole plot derived data

Material	E_r (Gpa)	E_u (Gpa)	k	h
Epoxy	0.09	1.76	0.09	0.54
As Rec	0.91	8.71	0.2	0.53
Alk-APS	0.98	8.38	0.19	0.54
Ox-APS	1.27	9.88	0.19	0.42

A significant reduction in the h value is observed in Ox-APS flax fiber composite when other flax fiber composites showed a negligible change compared with the pure polymer. It can be related to the blocking of the polymer chains mobility because of a strong interaction between Ox-APS and bio epoxy resin. Furthermore, introduction of flax fibers into the matrix increased the parameter k due to the blocking of polymer chains and subsequently relaxation processes. Parameter k is related the polymer chains relaxation processes in glassy region; thus, it is less sensitive to changes in interfacial adhesion and negligibly changed in silane treated composites [122].

4.6.3. Inter-Laminar Shear Strength

ILSS of as received and surface modified flax fiber reinforced epoxy composites are illustrated in Table 4.4. According to the results, as-received flax fiber composite exhibited the lowest inter-laminar shear strength due to weak interaction at fiber/matrix interface. ILSS of the composites is slightly changed (≈7 %) after Alk-APS treatment of flax fibers compared with as received one but this change is not statistically significant (P-value > 0.05). On the contrary, Ox-APS exhibited significant improvement (P-value < 0.05) in ILSS of the composite (≈12% compared to the as received composites). These results confirm that Ox-APS fibers form stronger interaction due to higher efficiency of silane treatment compared with Alk-APS fibers.

Table 4.4 Inter-Laminar Shear Strength as received and silane treated composites

Material		**ILSS (MPa)**	**SD**
As Received (I)		23.45	1.49
Alk-APS (II)		25.04	1.64
Ox-APS (III)		26.27	0.71
I,II	**Difference (%)**	7	
	P-value	> 0.05	
I,III	**Difference (%)**	12	
	P-value	< 0.05	
II,III	**Difference (%)**	5	
	P-value	> 0.05	

4.6.4. Flexural Strength

Flexural behaviour of as received and silane treated flax fiber composites are demonstrated in Figure 4.4 and the results are summarized in Table 4.5.

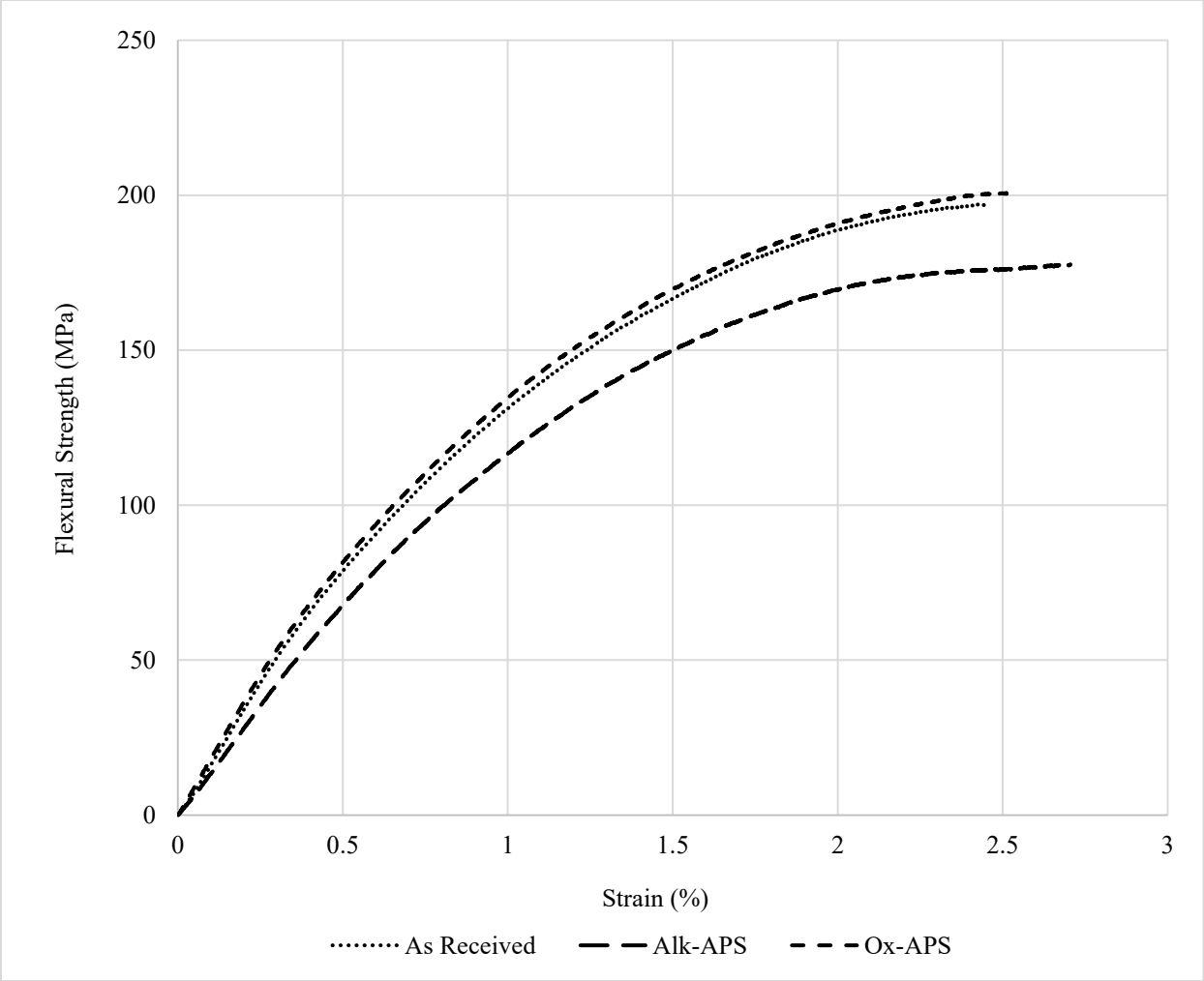

Figure 4.4 Flexural behaviour of as received and surface treated fiber reinforced composites

It was observed that flexural modulus and strength of flax fiber composite are significantly reduced after Alk-APS treatment. This reduction can be related to the removal of the non-cellulosic components of the fibers that act as a cementing material in the fiber cell walls by pre-treatments. Subsequently, this elimination enhanced the mobility and maximum deformation of cellulosic micro-fibrils and decreased the modulus [138]. In addition, partial degradation of fiber cell walls might occur during alkaline treatment that declined the fiber strength. However, the Ox-APS fibers showed a significant improvement in both flexural modulus and flexural strength compared with the Alk-APS. These improvements are attributed to the efficient silane treatment that enhances the fiber/matrix interaction as it also observed in storage modulus increment for Ox-APS composites [112]. An efficient silane

treatment might also blunt the defects and crack tips on the fiber and improves the mechanical properties of the composite [139].

Table 4.5 Flexural properties of as received and silane treated composites

Material		Modulus	SD	Strength	SD	Strain	SD
As Received (I)		16.9	1.3	198	11.8	2.4	0.14
Alk-APS (II)		13.1	1.0	172	7.3	2.7	0.12
Ox-APS (III)		17.9	0.4	202	5	2.5	0.15
I,II	**Difference (%)**	22.5		13.1		12.5	
	P-value	<< 0.05		< 0.05		> 0.05	
I,III	**Difference (%)**	5.9		2		4.1	
	P-value	> 0.05		> 0.05		> 0.05	
II'III	**Difference (%)**	36.6		17.4		7.4	
	P-value	<< 0.05		<< 0.05		≤ 0.05	

4.6.5. SEM analysis

Cross-sections of as received, Alk-APS, and Ox-APS flax fiber reinforced epoxy are shown in Figure 4.5. SEM micrograph of as received flax/bio epoxy composite (4.5a) showed wide gaps at the interface that is related to the weak adhesion between fiber and matrix. It seems that the Alk-APS treatment slightly improved the interaction at the composite interface and diminished the gap size between fiber and matrix (4.5b). As expected, the gap was minimized at the Ox-APS flax fibers composite interface (4.5c) that indicates the good interaction between fiber and matrix.

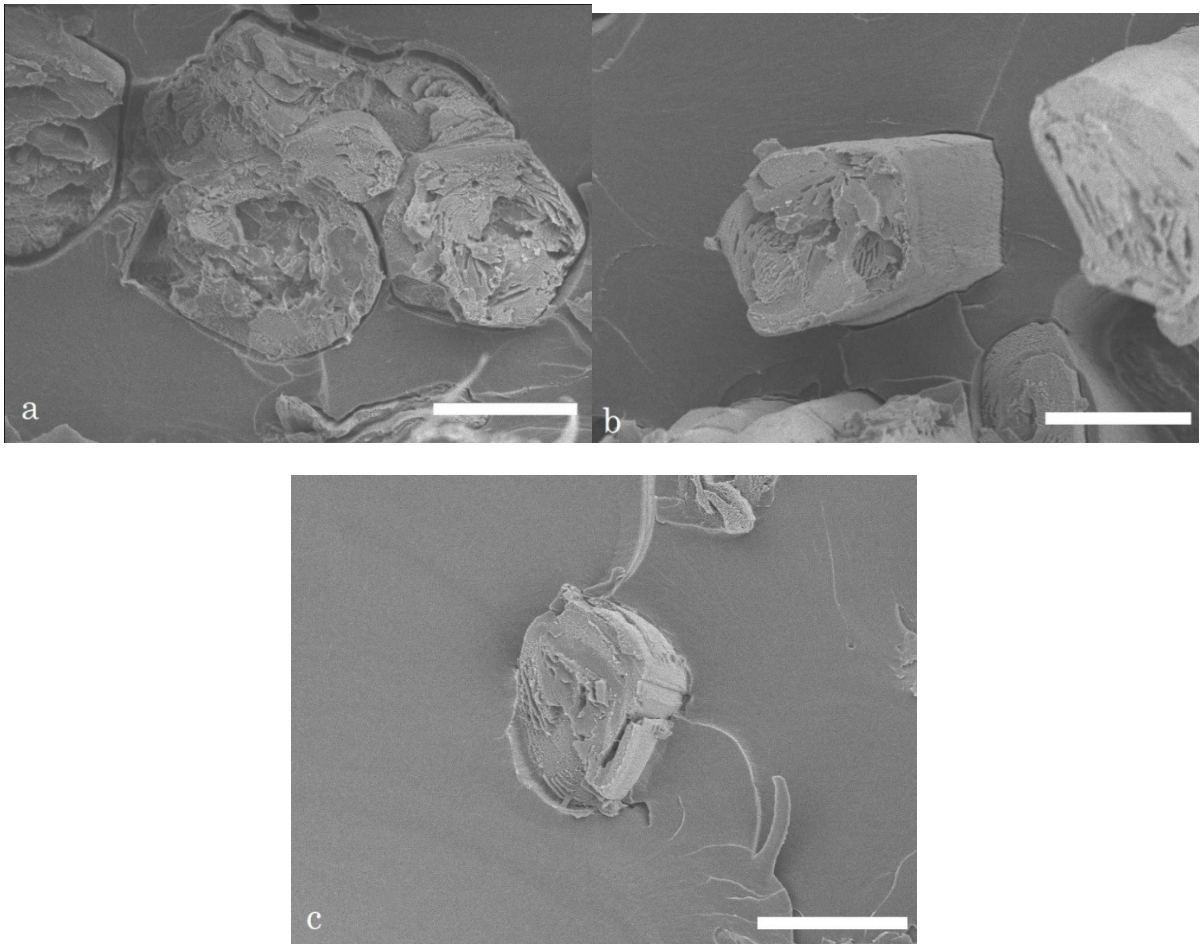

Figure 4.5 Cross-section analysis of fractured a) as received b) Alk-APS treated and c) Ox-APS flax fiber composites. The white bar scale length is 10 µm

4.6.6. Water Absorption

The water absorption of flax/bio epoxy composites, as a function of square root of time divided by thickness, is depicted in Figure 4.6. The curves showed that water uptake by all of composites linearly increased with square root of time and then decelerate until water saturation point. It can be seen that the slope of the curve decreases after surface modification of flax fibers. In addition, the water uptake of surface treated fiber composites are decreased compared to the as received fiber composite. The maximum water uptake M_∞, diffusion parameter (slope of the curve) k and coefficient of diffusion D are shown in Table 4.6. These reductions can be related to a decrease in accessible hydroxyl groups on the silane treated fiber surface that subsequently resulted in the lower hydrophilicity of fibers.

Table 4.6 Water uptake of as received and silane treated flax fiber composite

Material	As Received	Alk-APS	Ox-APS
Water Uptake (% wt.)	11.1	9.4	8.8
K (slope of linear part)	0.04	0.029	0.023
Coefficient of Diffusion (mm^2/sec)	2.55e-6	1.87e-6	1.54e-6

Furthermore, an improved interaction between silane treated flax fibers and bio epoxy resin reduces defects and gaps at the composite interface which significantly decrease the water absorption [140]. Maximum water uptake of Ox-APS and Alk-APS composites is decreased about 20% and 15% compared with as received composite. It confirms the efficiency of our novel approach for silane treatment of TEMPO oxidized flax fibers.

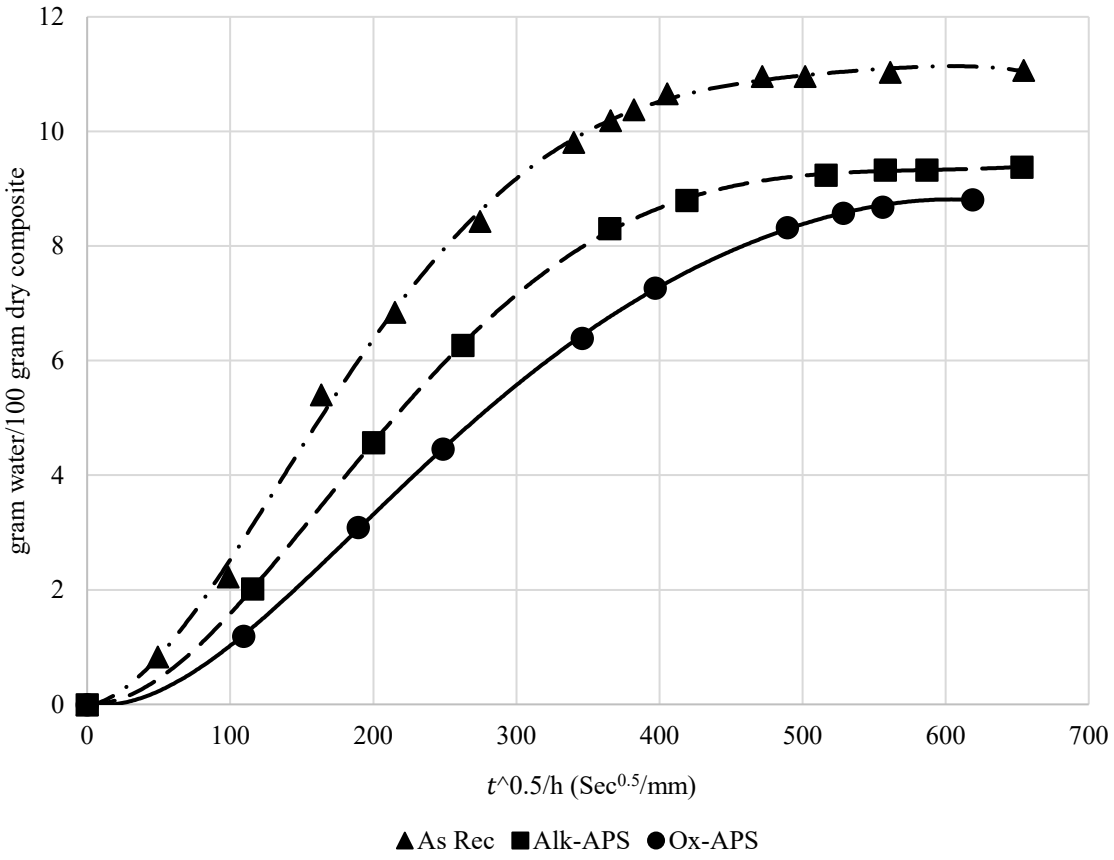

Figure 4.6 Water uptake curve of as received and silane treated composites

4.7. Conclusion

In this study we have presented a new approach to modify the interface between flax fiber and bio epoxy through the TEMPO oxidation of fibers followed by silane treatment. The Ox-APS flax fiber composite was compared with as received and Alk-APS treated ones. Dynamic mechanical analysis revealed higher compatibility at the interface of Ox-APS composite compared with Alk-APS composite. In addition, the defect concentration was decreased in Ox-APS and relaxation times of polymer chains increased which both are related to strong interaction between Ox-APS fiber and bio epoxy matrix. Furthermore, the ILSS of flax/bio epoxy composites confirmed the higher effectiveness of silanization treatment after oxidation compared to the Alk-APS treatment. In the meantime, flexural properties of Ox-APS were improved whereas they were decreased in Alk-APS composite. It might be caused by the aforementioned degradation/blunting mechanism, which affects the stress transfer between the fibers and the matrix. Eventually, the significant reduction in water absorption of the Ox-APS flax reinforced composite has proved the higher hydrophobicity of Ox-APS composite.

4.8. Acknowledgement

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5. Conclusion and Future Works

5.1. Conclusion générale

Ce projet de doctorat visait à étudier les paramètres qui influencent la qualité de l'interface des composites à renforts de fibres naturelles (lignocellulosiques) afin de mettre au point une procédure de modification des fibres naturelles pour la mise en œuvre de composites polymères. Les agents de couplage au silane ont été largement utilisés pour modifier la compatibilité entre les fibres lignocellulosiques hydrophiles et les matrices polymères hydrophobes. Cependant, les molécules de silane doivent être pré-hydrolysées pour interagir avec la surface des fibres naturelles et traitées thermiquement à la fin de la procédure. Dans cette étude, nous avons utilisé une nouvelle méthode pour augmenter la réactivité des groupes hydroxylés sur la surface des fibres de lin au moyen de l'oxydation TEMPO afin de faciliter le traitement ultérieur au silane.Pour cela, les couches faiblement liées, les composants non cellulosiques et les matériaux lipophiles présents à la surface des fibres ont d'abord été éliminés par prétraitement (déparaffinage et traitement alcalin). L'analyse FTIR a montré que le ratio de l'intensité des pics hydroxyle/méthylène était significativement plus élevé, ce qui confirme que le prétraitement des microfibrilles cellulosiques exposées a conduit à une plus grande accessibilité des groupes hydroxylés pour une fonctionnalisation/réaction ultérieure. Ensuite, afin d'augmenter la réactivité chimique de la surface de la fibre, les groupes hydroxylés de la cellulose ont été convertis en groupes carboxyliques par une oxydation TEMPO optimisée antérieurement. La création de groupes carboxyliques sur la surface de la fibre a été confirmée par titrage conductimétrique. Enfin, les fibres oxydées ont été traitées directement avec un agent de couplage silanique.

Les résultats XPS ainsi que l'analyse EDS ont montré que la capacité de de liaisonnement des agents de couplage silaniques avec les fibres oxydées était significativement plus élevée qu'avec le seul traitement alcalin.

L'ATG a révélé que le traitement d'oxydation alcaline et TEMPO n'a pas affecté négativement la stabilité thermique des fibres de lin. De plus, les résultats ATG et SFX (?) indiquent que les molécules de silane réagissent avec les fibres oxydées environ 5 à 6 fois plus que les fibres alcalines traitées.

L’analyse MEB a montré une meilleure adhérence entre la fibre de lin et la résine époxy après un traitement d’oxydation alcaline et TEMPO. Cependant, l’adhérence des fibres oxydées à l’époxy était significativement plus forte.

L’essai de traction des fibres traitées en surface a montré que toutes les méthodes de modification diminuent le module d’Young alors que la résistance à la traction augmente significativement. Cela serait dû à l’élimination des composés non cellulosiques des fibres qui conduirait au relachement des liaisons interfibrillaires et, par la suite, au réarrangement des microfibrilles de cellulose devenues plus mobiles dans une orientation plus compacte.

Finalement, afin d’évaluer la performance réelle des fibres traitées au silane dans les biocomposites un bioépoxy a été renforcé par des tissus de lin traités au silane. Le composite renforcé avec le lin traité au silane oxydé a montré une amélioration significative (12 %) de l’ILSS par rapport à celui reçu, tandis que le composite traité au silane alcalin n’a pas montré d’amélioration significative. Cela serait lié à la meilleure qualité de l’interface entre la fibre oxydée et la matrice.

De plus, le composite avec les fibres de lin oxydées et silanisées absorbe moins d’eau, ce qui peut être lié à la plus forte interaction fibre/matrice qui réduit la diffusion de l’eau.

Cette étude a donc permis d’améliorer l’efficacité du greffage des agents de couplage silaniques sur la surface de la fibre de lin et ainsi d’augmenter sa compatibilité les matrices polyméres, ce qui s,est traduit par une amélioration des performances mécaniques du composite bioépoxy de même qu’une réduction de l’absorption d’eau.

5.2. General Conclusion

This PhD project aimed to study the effective parameters of natural (lignocellulosic) fiber reinforced composite interface to develop a procedure to modify natural fibers for implementation in polymer composites. Silane coupling agents have been widely used to modify the compatibility between hydrophilic lignocellulosic fibers and hydrophobic polymer matrices. However, silane molecules should be pre-hydrolyzed to interact with natural fibers’ surface and should be heat treated at the end of procedure. In this study, we used a novel method to increase the reactivity of hydroxyl groups on the flax fiber surface by means of TEMPO mediated oxidation in order to facilitate the subsequent silane treatment.

For this purpose, weakly bonded layers, non-cellulosic components and lipophilic materials that exist on the fiber surface was first eliminated by pre-treatment (dewaxing plus alkaline treatment). FTIR analysis showed that hydroxyl/methylene peak intensity ratio was significantly increased. This means that the pre-treatment exposed cellulosic microfibrills led to higher accessibility of cellulosic hydroxyl groups for subsequent functionalization/reaction. Then, in order to increase the chemical reactivity of the fiber surface, the cellulose hydroxyl groups were converted into carboxylic groups by means of TEMPO mediated oxidation. The TEMPO oxidation conditions have been optimized by an earlier research in the group. The creation of carboxylic groups on the fiber surface was also confirmed by conductimetric titration.

Then the oxidized fibers were treated by direct application of a silane coupling agent. XPS results along with EDS analysis showed that the bonding efficiency of silane coupling agents on the oxidized fibers was significantly higher than alkaline treatment.

TGA revealed that alkaline and TEMPO oxidation treatment had not adversely affected thermal stability of flax fibers. In addition, TGA and XRF results indicated that silane molecules reacted with oxidized fibers about 5-6 times more than the alkaline treated fibers.

SEM analysis showed improved adhesion between flax fiber and epoxy resin after both alkaline and TEMPO oxidation treatment, however, oxidized fiber adhesion to epoxy was significantly stronger.

The tensile test of the surface treated fibers showed that all modification methods decreased Young modulus whereas the tensile strength significantly increased. This would be due to the elimination of non-cellulosic ingredients of the fibers which led to interfibrillar matrix softening, and subsequently, the free movement of cellulose microfibrills to rearrange themselves in a more compact orientation.

Eventually, in order to evaluate the real performance of the silane-treated fibers in the bio-composite, bio epoxy resin was reinforced by the silane-treated flax fabrics. The oxidized-silane treated flax reinforced composite exhibited a significant improvement (12%) in ILSS compared with the as received one while alkaline-silane treated did not show any significant improvement. This would be related to the better quality of the interface between the oxidized fiber and matrix.

Also, the oxidized-silane flax fiber composite showed a lower amount of water uptake. This would be related to the formation of a strong fiber/matrix interface that prevents the water to permeate inside the composite.

In general, the main objective of this study has been the development of a novel silane treatment method to remedy the drawbacks of natural fibers for bio-composite applications. The proposed method of this study has shown the enhancement of the fibers and the composites which have been reinforced by these fibers.

For the fibers, the effective grafting of silane coupling agents on the surface of the fibers was performed that increased the compatibility between fiber and matrix. Furthermore, the study has shown the performance of bio epoxy composite when it is reinforced by the modified fibers. The results showed a significant increase ILSS of the composite. Finally, this method improved the water uptake of flax fiber reinforced composite which is one of the main drawbacks in using of natural fiber polymeric composites.

5.3. Suggested Future Works

1. Comparative durability study of surface modified flax fiber composite in saline and alkaline environment

   The main objective of this work is to fabricate silane treated fiber reinforced epoxy composite and to investigate its effect on mechanical and physical properties after aging in saline and alkaline water (To simulate seawater and concrete medium conditions, respectively). The proposed methodology could be consist of:

   I) Fabrication of Oxi-Silane flax fiber reinforced epoxy as described in chapter 4.
   II) Conditioning the composites in saline and alkaline solution and monitoring the changes in mechanical properties of composites such as flexural, ILSS and impact strength

2. Using Polycarboxylic acids (PCAs) as a coupling agent for cellulosic fiber reinforced epoxy composites

   Poly carboxylic acids (e.g. butane tetra carboxylic acid (BTCA), citric acid, maleic acid) have used in textile industry for surface modification of cellulosic fibers through crosslinking of hydroxyl groups. Also, they have used as a hardener for the crosslinking

of epoxy resin. The ability of PCAs for reaction with both cellulose and epoxy resin make them a possible coupling agent for natural fiber reinforced epoxy composites. The suggested methodology could be consist of:

I. Finding optimum condition for surface medication of natural fiber with variety of PCAs through adjusting the type and concentration of poly acids plus time and temperature of reaction.
II. Optimizing the crosslinking reactions of epoxy resin by PCAs.
III. Implementation of as received and PCAs modified fibers in the neat and PCAs modified epoxy resin
IV. Characterization of physical and mechanical properties of the composites such as Tensile, Flexural and Impact strength besides water uptake.

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